UNIVERSITY OF CAPE TOWN

An investigation of CCA-treated wood in informal caterers' fuel stocks and related airborne arsenic in the Cape Town region

A dissertation submitted in partial accomplishment of the requirements of Master of Science in Engineering degree.

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Declaration

I know the meaning of plagiarism and declare that all work in this document, save for that which is properly acknowledged, is my own.

This is has not been submitted for any degree or examination in any other university.

Signed:.....Rissa

Rissa Vénérande Niyobuhungiro

Date: March 2012

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Synopsis

In developing countries, energy poverty remains a challenge, impacting on the environment, health, security and well-being of an estimated 3 billion people. Fuel wood remains an important but environmentally problematic fuel in this context. The urban poor are known to make use not only of harvested but also of waste timber. Prior studies in Cape Town indicated substantial uses of fuel wood by informal communities for thermal requirements, such as cooking and heating by both households and informal and formal caterers. Waste wood may be recovered from disposal systems or landfill sites, or sold on second hand markets, forming an interface to the informal settlement wood market.

Much of the timber used in construction or agricultural activities in South Africa is treated with wood preservatives, with chromated copper arsenate (CCA) being the most widely used chemical. This informed the central research question addressed in this dissertation, viz. whether such CCA-treated wood is used in informal economic activities, in particular street catering. Of particular concern was that when CCA-treated wood is burned, chemicals, mainly arsenic, might be released into the environment in the form of particulate matter (PM). Arsenic is a known carcinogen and the targets organs are lungs, bladder and liver. It can also affect reproductive organs, especially in women.

This dissertation therefore aims to determine whether, and how, informal urban caterers and their clients are exposed to toxicity risks arising from Chromium, Copper and Arsenic in their fuel-wood. The investigation is structured around the following objectives:

i. Determine that CCA containing wood is used,
ii. Determine how much Chromium, Copper, and Arsenic it contains,
iii. Determine the concentration of the metals in the smoke produced.

A total of six places from both urban and peri-urban areas in and around Cape Town were studied, including Nyanga, Langa and Khayelitsha as typical urban cases, and Kayamandi (Stellenbosch), Zwelethemba (Worcester) and Mbekweni (Paarl) as representing peri-urban settings. Sampling was done in three different sampling campaigns. 116 wood samples and 18 smoke samples were analysed for copper, chromium and arsenic content. Wood samples were reduced to sawdust and then digested by microwave using nitric acid (55 %). The digests were analysed by ICP/AES.

The randomly conducted first sampling campaign in Nyanga and Khayelitsha identified no cases of CCA-treated wood amongst 86 analysed samples, with the indicative concentrations of 11.8 ± 11.6, 11.0 ± 4.6 and 6.2 ± 3.0 mg/kg of Cr, Cu and As likely to reflect the natural background levels.

The mean Cr, Cu and As levels in eight samples identified as treated amongst twelve that were purposefully taken for their appearance from peri-urban areas collected in second sampling campaign were 1946 ± 2123, 849 ± 592 and 1427 ± 1167 mg/kg of Cr, Cu and As, respectively. During the third sampling campaign, eight samples were also positively identified to have the mean Cr, Cu and As levels at 2035 ± 917, 871 ± 344 and 1645 ± 710 mg/kg, respectively, and were found in both urban and peri-urban fuel wood stock piles.

The average of the PM_{10} concentrations determined in smoke samples close to street caterers working with open fires was 1685 $\mu g/m^3$. The lowest concentration was found around the Nyanga taxi rank at a distance of ±100 m from caterers, at 33 $\mu g/m^3$, while the highest concentration was 8139 $\mu g/m^3$ for a 1-hour sample representing occupational exposure close to wood burning fires. Arsenic was detected in 15 smoke samples with the lowest concentration being 0.1 and the highest 11.8 $\mu g/m^3$ of arsenic. The average of the arsenic positive samples was 1.3 $\mu g/m^3$ of arsenic.

Under controlled conditions, it was noted that the concentration of arsenic volatilised from typical CCA-treated wood ranged between 19 and 52 $\mu g/m^3$.

The smoke samples results from this investigation revealed that levels of arsenic from 0.1 to 11.8 $\mu g/m^3$ exceed normal background levels, which have been reported to be 0.02-4 ng/m^3 in rural and up to 30 ng/m^3 in urban air (WHO, 2000). Those smoke samples results also showed that high arsenic levels were found near fires in which CCA- treated wood were found.

The dissertation concludes that CCA-treated wood is being used in informal catering activities both in Cape Town townships and in peri-urban areas of the Winelands district. In city townships, the occurrence of such timber appears to be rare (estimated to be of the order of 0.1-1%) and only be detectable by a trained eye as it generally is old timber; even so, only 5 out of 14 suspected samples tested positive for CCA. In peri-urban areas, CCA-treated timber was more frequently encountered in fuel stocks (estimated at 1-90%), and clearly distinguishable by its colour and young age.

The following recommendations are made:

- Further research work in this field should proceed by statistical sampling in order to determine more precisely the frequency of occurrence of CCA-treated wood.
- Further investigation should also emphasise arsenic speciation in the smoke as this determines the human toxicity risk to a significant extent.
- Ash produced by informally operating caterers should also be further studied, and their ash waste management practices be reconsidered in the light of possible toxicity risks.

- Arsenic-free wood treatment chemicals should be promoted.
- The South African wood preservation industry should consider new ways of interpreting product stewardship, to address this thus far unknown end-of-life utilisation of their product.
- The government should consider regulating separate collection of CCA-containing waste wood.
- The government should also educate citizens about the dangers of wood burning especially for post-use waste wood.
- Government and industry should encourage consumers of fuel wood to stop buying CCA-treated wood. In particular, caterers in the informal economy should not use CCA-treated wood under any circumstances, and they should be alerted that it can be recognized it by its olive-green coloration.

Table of Contents

List of Tables

List of Figures

Abbreviations

ACC:	Acid Copper Chromium
ACQ:	Alkaline Copper Quaternary
AWPA:	American Wood Preserves' Association
BUP:	back-up pad
CBA:	Copper Borate Azole
CC:	Copper Citrate
CCA:	Chromated Copper Arsenate
CDDC:	Copper diethyldithiocarbomate
Cu-8-Q:	Copper-8- quinolinolate
CZC:	Chromated Zinc Chloride
C&D:	Construction and Demolition
EBE:	Engineering and the Built Environment
EHC 224:	Environmental Health Criteria 224
EiRC:	Ethics in Research Committee
FP^3:	Fine Particle Pollution Program
ICP/AES:	Inductive Coupled Plasma/Atomic Emission Spectrometry
MCE:	mixed-cellulose ester
MOE:	Ministry of Environment
MSW:	Municipal Solid Waste
OSHA:	Occupational Safety and Health Administration
PEL:	permissible exposure limit
PM:	Particulate Matter
PMRA:	Pest Management Regulatory Agency
PTFE:	Poly tetrafluoroethane
SA:	South Africa
SABS:	South African Bureau of Standards

SANS:	South African National Standard
SAWPA:	South African Wood Preservation Association
TAS:	Tactical Air Sampler
TCLP:	Toxicity Characteristics Leaching Procedures
TD4SUD:	Technology Deployment for Sustainable Urban Development
TEOM:	Tapered Element Oscillating Microbalance
TLV/TWA:	threshold limit value/time-weighted average
UK:	United Kingdom
UN:	United Nations
USA:	United States of America
US EPA:	United States Environmental Protection Agency
WHO:	World Health Organization

1 Introduction

1.1 Background

Solid waste management is one of the biggest challenges for the many cities of developing countries, having a direct impact on quality of life and the natural environment. Many cities of the developing countries do not have effective solid waste management systems in place, particularly in their poorest areas, their informal settlements, which are marginalised and underserviced. As solid waste can pose a significant threat to the ecological, health, social and economic integrity of an urban community, effective solid waste management holds great potential for promoting a cleaner living environment and local community development for the people.

Rapid urbanization and inadequate capability to cope with the housing needs of people in urban areas, have contributed to the fast development of informal settlements in the world.

The definition of informal settlements is context-specific, but the definition suggested by the UN Habitat Programme is probably the most applicable.

Informal settlements are defined as:

i) Residential areas where a group of housing units has been constructed on land to which the occupants have no legal claim, or which they occupy illegally;

ii) Unplanned settlements and areas where housing is not in compliance with current planning and building regulations (unauthorized housing).

In the Western Cape Metropolitan, the informal settlements represent approximately 42% of the total housing backlog (Goven, 2007). Cape Town alone has a large number of informal settlements which are located at the periphery of the inner city, "We also have a housing waiting list of about 460,000 and 222 informal settlements around the city (150,000 shacks compared with 28,000 in 1994), and a growing crime rate," Cape Town Mayor - Helen Zille. April 10 2008

There is nodal overpopulation in informal settlements, comparing to that in formal housings areas. For example, approximately 2 million people live in informal settlements and slums in Nairobi. These people account for over half the capital's population, yet are crammed into only five per cent of the city's residential area and just 1 per cent of all land in the city. This high population density has serious health implications, with access to clean water and sanitation a prominent concern featuring

in the UN Millennium Development Goals to be met by 2015. Air pollution is another major concern. Cooking and heating facilities are inadequate in informal settlements; the majority uses cheap or free fuels such as wood, charcoal or grass, with the consequence that there are high levels of exposure to both indoor and outdoor pollution. This, in turn, is associated with a number of serious respiratory, cardio-vascular and skin lesions diseases. When the burden of disease is already high, particularly with respect to HIV/Aids, tuberculosis and malaria, air pollution becomes an additional contributor to morbidity and mortality (Zar, 2010). This problem has influenced generations of research and development focused on "appropriate technology", particularly for household energy uses (Muchiri and Sengendo, 1999). It has arguably been too inward-focused and charitable, ignoring the possibility of rising out of poverty through economic participation.

The informal economy is a major contributor to production, consumption, employment and earnings generation in the developing world. It is a source of livelihood for a majority of people who do not have proper social safety-nets and unemployment insurance such as poor, unskilled, and socially marginalised as well as the female population (Yadav, 2009; Hiralal, 2010).

Catering, which requires fuels for food and drink preparation, is a common informal business in both informal and formal settlements. The lack of access to modern fuel sources is one of the causes of slow business growth, negative health impacts and pollution (Rasmussen et al., 2007). Inefficient use of available energy sources may be another contributor to these problems.

In developing countries, energy poverty remains a challenge, impacting on the environment, health, security and well-being of an estimated 3 billion people. Around 2.64 billion people, or 40% of the world's population, lack adequate fuels for cooking and heating, while 1.6 billion have no access to electricity, three-quarters of them living in rural areas (Balmer & Hancock, 2009). To raise the profile of these challenges, the United Nations General Assembly has declared 2012 as the International Year of Cooperatives, highlighting the contribution of cooperatives to socio-economic development. The Assembly noted that cooperatives have a positive impact on poverty reduction, employment generation and social integration, (Llamas, 2009).

As discussed above, these challenges affect not only people in rural areas but also people who live in poor urban areas.

When there is simultaneously a scarcity of fuels and a lack of effective waste management, under informal living and production conditions as sketched out above, it is likely that combustible wastes will be used as fuel. This applies particularly to waste wood.

This argument is supported by estimates for wood waste management in Cape Town, which reported that 142 000 tonnes per annum of waste wood is used by informal communities for thermal requirements, such as cooking and heating by both households and informal and formal caterers (Nissing & Von Blottnitz, 2007).

In Cape Town, where households even in informal settlements have reasonable access to other energy sources such as paraffin, gas and electricity, the primary consumption of such wood for fuel happens at commercial meat grilling places in informal settlements. This fuel consists of both harvested wood and waste wood. The latter is often treated with chemicals and disposed of into Municipal Solid Waste (MSW), although illegal dumping, particularly of builders rubble, around the informal settlements remains of concern (Goven, 2007; Nissing and Von Blottnitz, 2007).

The City of Cape Town has an active air quality management plan and system, which recognizes that the major source of air pollutants include vehicle emissions and fugitive dust from roads, industry, agriculture, construction and demolition, and fly ash from fossil fuel combustion (City of Cape Town, 2007; Fierro, 2000; Nissing and Von Blottnitz, 2007). Tellingly, however, wood fires (along with wind-blown dust) are the major contributors to the air pollution in Khayelitsha, (City of Cape Town, 2007). This wood burning in Khayelitsha is recognised to be dominated by the food preparation activities of caterers.

In South Africa, significant volumes of wood entering the economy are treated with wood preservatives. The South African Wood Preservation Association (SAWPA) produces statistics which show that of the total volume of wood used in 2010, treated wood accounted for 850 670 m^3. Among the treated volume, 523 657 m^3 (61.5%) was by chromate copper arsenic (CCA) and 320 277 m^3 (37.6%) by creosote, with the remaining 0.90 % covered by other treatments (Breedt, 2012).

Amongst the ingredients of CCA, Arsenic is a known cancer-causing element with its target organs being lungs, the bladder and the liver. It can also affect reproductive organs, especially in women, (Kopaj, 2004; WHO, 2003). Arsenic is a metalloid solid, which sublimates, with a normal boiling point of 613 °C from the periodic table of elements, so is likely to be released with smoke when CCA-containing wood is burnt as seen by Kakitani et al (2004). SAWPA warns explicitly that the CCA-treated timber should never be burnt, (SAWPA, 2012)

1.2 Problem Statement

Informally operating street caterers work in environments where both waste management and air quality management might be poor or absent, and are known to use both harvested and waste wood for fuel. Since significant volumes of wood entering the economy are treated, it is not unreasonable to suspect that some of their fuel wood may contain the toxic chemicals in CCA. The concern is that when CCA-treated wood is burned, chemicals, mainly arsenic, are released into the environment in the form of fine particulate matter (PM), which may be inhaled, causing ill health.

This current investigation focuses on the possibility of metal pollution arising from the use of Chromated Copper Arsenate (CCA) treated timber by informal economy caterers, in selected urban and peri-urban areas of Cape Town.

1.3 Objectives

The end of the normal use of CCA-treated wood represents a source of energy and metals, but simultaneously poses a disposal threat due to the toxicity of arsenic and chromium. In the present study, we want to determine whether, and how, informal urban caterers and their clients are exposed to toxicity risks arising from Chromium, Copper and Arsenic in their fuel-wood when they burn this.

To investigate this potential risk in the work environment of informal urban caterers, three specific objectives are set:

i. Determine that CCA-containing wood is used,
ii. Determine how much Chromium, Copper, and Arsenic it contains,
iii. Determine the concentration of the metals in the smoke produced.

1.4 Scope of the study

As people living in informal settlements in developing countries generally face similar socio-economic challenges (WHO, 2008), this investigation focuses on some identified Cape Town settlements as indicative of other settlements in Africa. With wood treatment regimes primarily defined at national level, findings for Cape Town should be readily transferable to other informal economy activities across the country. Nyanga, Khayelitsha and Langa represent the settlements in urban areas, while Kayamandi (Stellenbosch), Worcester and Mbekweni represent the settlements in peri-urban areas. These will be introduced in more detail in Chapter 3.

Focusing on the Caterers environments, this study investigates the potential exposure of both caterers and their clients to Arsenic, Chromium and Copper by studying the frequency of occurrence and levels of treatment in fuel wood, and the levels released into the atmosphere when the wood is burned.

1.5 Significance of the study

This study will help to develop an understanding of the environmental and health hazards arising from the use of CCA-treated wood. It will help to develop an understanding of the characteristics of pollutants from CCA-treated wood as a fuel, so as to develop an appropriate policy for the CCA-treated wood disposal and management as a solid waste in South Africa and other countries. This will enhance a healthy and clean environment and improve welfare of the community.

Furthermore, this study could form the basis for research in other developing countries, as it is a common practice for informal caterers to use wood as a fuel source.

1.6 Overview of the dissertation

This dissertation begins with a review of the available literature, related to the objectives of this investigation, presented in Chapter 2. This provides an overview of CCA wood treatment and its purpose, since its first use in 1933 to date. Related literature from other countries is also presented for comparative purposes. The chapter also details the environmental and health effects of the CCA treated wood and overviews the occurrence and toxicity of each of the three chemical elements

constituting the CCA treatment. Air pollution from the combustion of CCA treated wood is also reviewed, and standards and guidelines to handle and manage CCA treated wood are identified.

Chapter 3 presents the research motivation and the research questions. The methodology adopted to answer the research questions is then developed. Next, the sites selected for sampling are identified and described. Finally, the sample collection approach and laboratory methods are discussed.

The results are presented in Chapter 4, first for metal concentrations in collected wood samples, then for levels of PM_{10} and of arsenic in the air.

Based on the results presented in Chapter 4, Chapter 5 discusses the use of CCA-treated wood in urban and peri-urban areas. The air quality over the investigated areas and close to wood burning by different caterers is also discussed in Chapter 5. Furthermore, the link between the lack of access to improved fuel and the exposure to CCA wood is examined in the same Chapter.

Chapter 6 extracts the conclusions from the study and presents recommendations drawn accordingly.

2 Literature review

The literature review describes wood preservation in general, and specifically with chromated copper arsenate (CCA) in South Africa. It describes the occurrence and toxicity of the investigated metals, and airborne particulate matter as one form in which these metals potentially occur in the environment when CCA-treated wood is burnt. Finally, it gives an overview of the contribution of the investigated metals to air pollution and lung diseases.

2.1 Wood preservation

The measures taken to prolong the life of wood fall under the definition: **wood preservation**. Wood preservatives are chemical compounds used universally in the wood industry. No timber is resistant to deterioration if not protected, preservative treatment is important for prolonged service life of the product and for enduring results in the industry (Hay et al., 2000).

The history of wood preservation started in the 1830s (Hay et al., 2000). Since then, various processes have been introduced or improved. Today, preservation techniques ensure a deep and uniform penetration of preservatives. Both pressure processes and non-pressure processes are used. The most common application processes today is the impregnation under pressure. Many wood types can be efficiently treated, but some species are very resistant. However, the treatment of such wood has been successfully achieved by first cutting into the wood to facilitate penetration. This has a higher cost and sometimes compromises the quality of the wood (Wolman, 2008).

2.1.1 Pressure treatment process

Pressure processes are the most stable methods used today in extending timber life. In a typical pressure treatment process, wood is placed in a horizontal cylinder. The cylinder is flooded with the chemical followed by a cycle of pressure and vacuum.

These processes have a number of advantages over the non-pressure methods. In most cases, a deeper and more uniform penetration and a higher absorption of preservative is achieved (Wu et al., 2004; Solo-Gabrielle et al., 2002; Wolman, 2008). Another advantage is that the treating conditions can be controlled so that retention and penetration can be varied. The high initial costs for equipment and the energy costs are the biggest disadvantages of the pressure treatment.

2.1.2 Non-pressure processes

The non-pressure processes of treating wood vary primarily in their procedure. The most known of these treatments involve the application of the preservative by means of brushing or spraying, dipping, soaking, steeping or by means of hot and cold bath. There is also a variety of additional methods involving applying preservatives in bored holes, diffusion processes and drain displacement. Those processes were not maintained because of their low diffusion which causes the easy washing off of the preservatives (Wolman, 2008).

2.1.3 Classification of wood preservatives

There are different classes of wood preservatives, depending on their use and their risks. Quite few are briefly described below.

Acid copper chromate (ACC)

Wood preservatives containing ACC are only registered for industrial and commercial use. ACC treated wood contains hexavalent chromium which is in the highest EPA toxicity category for oral, dermal and inhalation toxicity and is also a skin sensitizer. Protective equipment is usually required when producing or handling ACC treated wood (NPIC, 2011).

Alkaline copper quaternary (ACQ)

ACQ wood preservatives (type A, B, C and D) are composed of copper oxide and quaternary ammonia compound. The absence of chemicals like arsenic or chromium has made ACQ one of the most widely used residential wood preservatives (NPIC, 2011).

Borates

Borate wood preservatives are composed of naturally occurring minerals that protect wood from fungus, termites, and other wood-decomposing organisms. Borate wood preservatives are comprised of disodium octoborate tetrahydrate. Borate wood preservatives are low-toxicity treatments used primarily on indoor wood that is protected from weather (NPIC, 2011).

Chromated Copper Arsenate (CCA)

Chromated copper arsenate (CCA) wood preservatives contain chromium, copper and arsenic. Pressure-treated wood containing CCA is no longer used in most residential settings. The chemicals

in CCA-treated wood have been shown to leach into the surrounding environment and can transfer to the skin when people touch the wood (NPIC, 2011).

Copper Azole (CA)

Copper azole-treated wood is greenish-brown and has little to no odor. Type A (also known as CBA-A) contains copper, boric acid, and tebuconazole. Type B (also known as CA-B) contains higher concentrations of copper and tebuconazole but no boric acid. Copper azole is registered for a variety uses above and below ground, as well as in freshwater and marine decking applications (NPIC, 2011).

Creosotes

Creosote-treated wood has either a thick black mixture of coal tar chemicals on the wood or the clear to yellowish greasy resin of the creosote bush. Many railroad ties are treated with creosote or pentachlorophenol. Creosote-treated wood can leach chemicals that may dissolve in water, move through soil and contaminate groundwater. Creosote can also be taken up by plants and animals and is considered a probable human carcinogen. Creosote-treated wood may only be used in commercial applications; there are no residential uses for creosote-treated wood (NPIC, 2011).

Light Organic solvent preservatives (LOSPs)

LOSPs are specialised treatments, generally for higher cost commodities like joinery. They may contain fungicides, insecticides and water repellent chemicals (not necessarily all at once). They are applied in sophisticated treatment plants and usually provide a protective envelope of treatment around the fabricated product. They are not intended for use where the treated commodity comes into contact with the soil (Greaves et al., 2005)

This study investigates only the chromated copper arsenate.

2.2 Chromated copper arsenate preservative

Chromated copper arsenate (CCA) is an inorganic waterborne additive commonly used in the wood preservation industry to prevent environmental degradation and to prolong the service life of wood as a building material (Khan *et al.*, 2004). CCA has been used to pressure-treat wood intended for outdoor uses, including decks, picnic tables, playground equipment, telephone poles and docks. CCA has been preferred for timber treatment because it is economical, leaves a dry paintable surface and tends to become relatively leach exigent, (Moghaddam & Mulligan, 2008).

CCA was invented in 1933 by Kamesan in India as a wood preservative, is internationally established and has been used extensively worldwide since 1977, and in certain countries even earlier (Hay et al., 2000; Breedt, 2010). Since its invention, many types of CCAs have been introduced, and nowadays the most used formulation contains a mixture of arsenic pentoxide (As_2O_5), chromium trioxide (CrO_3), and cupric oxide (CuO). There are three general types of CCA, which differ in the content of each component, as shown in Table 2-1, (Khan *et al.*, 2004; Hay et al., 2000).

Table 2-1: Types of Chromated Copper Arsenate (CCA) Wood Preservatives

(Source: Solo-Gabrielle & Townsend, 1998; Hay et al., 2000; Khan et al., 2004; Wu et al., 2004; Wu et al., 2006)

TYPE	CrO_3 (%)	CuO (%)	As_2O_5 (%)
CCA-A	65	18	17
CCA-B	35	20	45
CCA-C	47.5	18.5	34

CCA-Type C is the most common type used in the USA and many other countries (Solo-Gabrielle & Townsend, 1998; Khan et al., 2004; Mayes, 2008). Breedt (2010) reported that CCA treated wood has been used in South Africa and New Zealand for more than 30 years, Australia 50 years and almost 70 years in the USA. In South Africa, New Zealand and Australia, it is designated for use in hazard classes H1 to H6, while in the USA and many other countries, it is used as CCA type C (Read, 2003).

The copper in the wood serves as the fungicide, while the arsenic protects the wood against insects and the chromium fixes the copper and arsenic to the wood.

Freshly CCA-treated wood shows a dark green colour which over time changes to grey with weathering, making it indistinguishable from untreated wood (Figure 2-1) (Read, 2003; Martin, 1998).

Figure 2-1: Wood waste at a construction and demolition debris recycling facility containing CCA- treated wood (Hinkley, 2003).

Recent research reports the dangers of CCA-treated wood in terms of leaching in rain water, when in normal use, and different contamination at the end of its normal use. All the effects meet in the pollution of the environment and thus the injuries to human life.

2.2.1 CCA treated wood in South Africa

In South Africa, as many other countries, CCA-treated wood has been used for many years.
In South Africa, of the 127 wood treatment plants certified by the South African Bureau of Standards (SABS), 112 are CCA preservative users, which clearly indicates the importance of CCA as a preservative chemical. All of them treat the wood in accordance with the relevant compulsory South African National Standards (SANS 10005) (Breedt, 2010).

In South Africa, CCA is applied only by industrial high pressure treatment processes. The treated wood has a wide variety of end uses, and is generally used outdoors, e.g. for decking, pole structures, landscaping, fencing and building structures. CCA is also extensively used for the preservative treatment of ground pole products and agricultural end uses. In South Africa, the softwood poles of the *Pinus* species (when used in the proclaimed areas) and hardwood poles, mainly from the *Eucalyptus* species (when used country wide), should be CCA-treated when used in structural applications (Breedt, 2010).
In South Africa CCA treatment is also extensively used as the preferred preservative in softwood sawn timber used in timber frame houses as well as in all roof structures in the proclaimed areas (SANS 10005) along the coastal belt.

2.2.1.1 *Classes of CCA treated wood types used in SA*

The South African Bureau of Standards (SABS) has set South African National Standards (SANS) for different categories of wood to ensure it remains protected against parasites and thus suitable for intended applications over long periods of time. The minimum CCA levels required to preserve timber for 20 years are shown in Table 2-2.

Table 2-2: Hazard class, CCA dosage and Application

(SANS 10005/SABS 05).

Wood category	Dose of CCA	Application
Hoi	None (Only insecticide)	Insecticide protection for specific purpose internal joinery (Moulings, Ceilings, Flooring)
H2	6 kg/m^3	Internal use (Frames, Roof Trusses and Ceilings)
H3	8 kg/m^3	Exterior above ground- moderate Hazard (Garden furniture, balustrades, Gates and Weather Boards)
H4	12 kg/m^3	Ground contact - High Hazard (fencing, pergolas, carports, bridges and flower boxes)
H5	16 kg/m^3	Fresh Water contact - High Hazard (Piling, Jetties, Retaining walls and walkways)
H6	24 kg/m^3	Sea water contact- High Hazard (Piling, Jetties, Slipways, Retaining Walls)

2.2.1.2 *CCA treated wood volumes produced in SA*

Breedt (2010) reported that the volume of all treated timber produced during 2008 in South Africa came to an estimated total of 1 032 000 m^3 of which 439 000 m^3 was treated sawn softwood timber and 593 000 m^3 was treated pole products.

Of these volumes, CCA-treated softwood timber and CCA-treated pole products contributed to 425 000 m^3 and 224 000 m^3 respectively, totalling 649 000 m^3, which relates to 62.9% of all timber treated in South Africa in 2008. The remainder of the 37.1% was made up of 364 000 m^3 of creosote-treated timber, 7 000 m^3 of boron-treated timber, 11 000 m^3 of LOSP (light organic solvent preservatives) treated timber and other alternatives (Breedt, 2010).

The volume of CCA treated timber decreased significantly from 2008 to 2009 by 223 613 m^3 (52.5%) and CCA (sawn and round) increased by 98 270 m^3 (23%) from 2009 to 2010 (Figure 2-2) (Breedt, 2012).

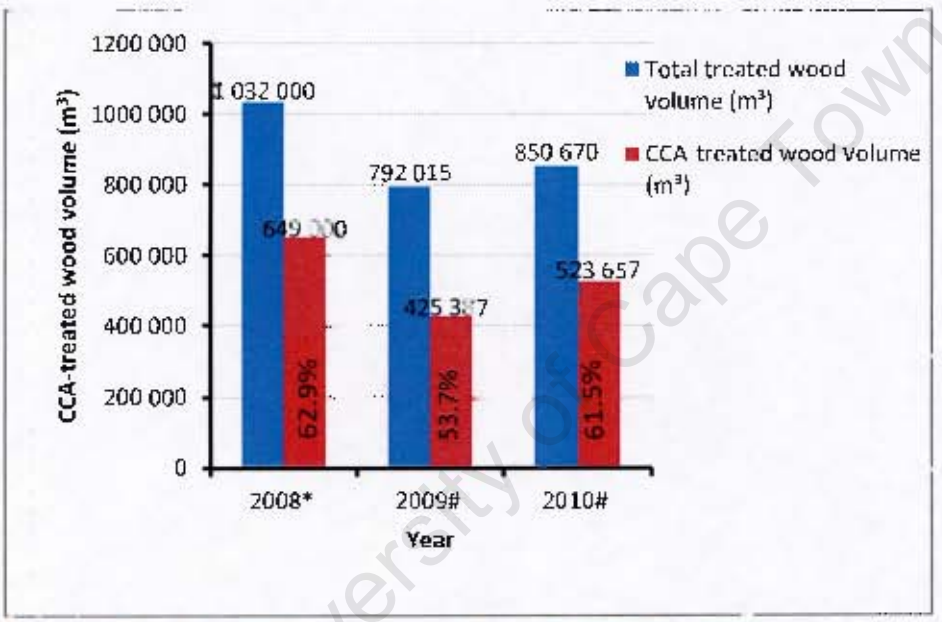

Figure 2-2: The volume of CCA treated wood produced in 2008, 2009 and 2010.

*: based on chemical sales

#: based on recorded volumes

Source: (Breedt, 2012)

2.2.2 Exposure to CCA

With CCA-treated wood, people can be exposed to harmful chemicals in different ways, as shown in Figure 2-3. Preservative treated wood contains components that may be toxic to non-target organisms if released into the environment in sufficient quantities (Lebow et al., 2004).

In a report done by Breedt (2010) from SAWPA, it is stated that it is safe to have contact with CCA-treated wood and that exposure to Arsenic is normal, as people are exposed to it in normal life as from food (fish) and drinking water. However, many other researchers reported the dangers of CCA-treated wood when people have contact with it. For example, children playing in jungle gyms made of treated wood are exposed to at least a dose of 7 µg/day (Martin, 1998). The acute lethal dose of inorganic arsenic to humans has been estimated to be about 0.6 mg/kg/day, (Martin, 1998).
A lethal dose of Arsenic can also be achieved by a cumulative process over two months. Multiple sub-lethal doses received over a period of several weeks can accumulate in the body to achieve a lethal dose. Sufficient research has not been done yet on the dangers of long-term exposure of low dose exposure (Martin, 1998). The WHO (2000) states that there is no safe concentration of arsenic to get exposed to.

It is also clear from many research studies that people may be exposed to the sawdust, or the smoke when burning CCA treated wood (Figure 2-3), unless special guidelines are considered.

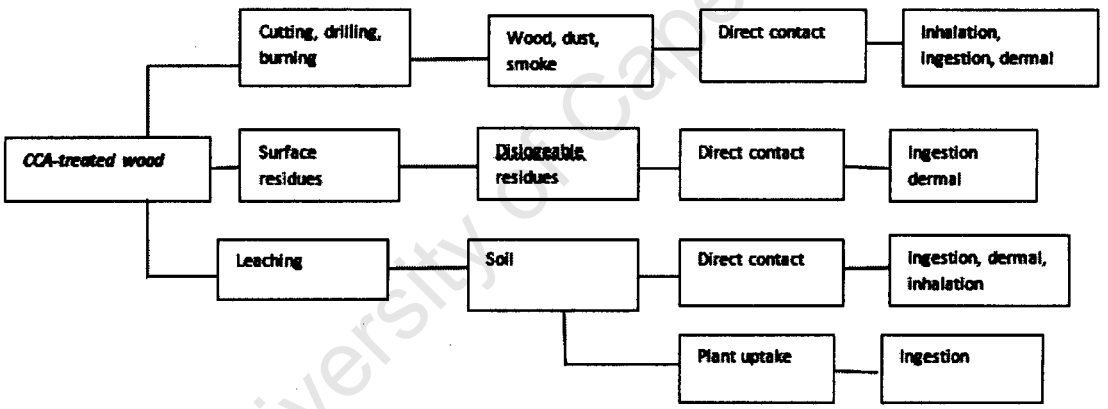

Figure 2-3: Possible routes of exposure to CCA

(Read, 2003)

2.2.3 CCA leaching from treated wood

Most leaching studies on CCA-C treated wood have shown that arsenic and copper leach to a greater extent than chromium when exposed to fresh water, (Moghaddam &Mulligan, 2008) and also arsenic was detected on the surface of treated products and in the soil below CCA-treated wood structures in use (Greaves, 2005; Solo-Gabrielle et al, 2004).

CCA is the most common wood preservative used in New Zealand and has been widely used since the 1950s.

In New Zealand, wood is also treated to hazard classes (H1-H6) although H1 and H2 are not commonly used (Mayes, 2008). CCA preservatives are approved for use in all hazard classes. The timber most commonly used for residential purposes is in classes H3 and H4. Timber for decks and garden furniture would typically be H3 with H4 for deck support posts in the ground and timber for playground equipment in the ground a mixture of H3, H4 and H5, depending on the local soil conditions and the equipment being supported on piles. H3 and H4 treated timber contain 0.11% and 0.22% arsenic per oven dry wood weight respectively (Read, 2003).

Read (2003) reported that from studies done on the leaching of CCA from natural rain events arsenic leached more than copper and chromium. Average soil levels from decks were 43 mg/kg for chromium, 75 mg/kg for copper and 76 mg/kg for arsenic and the concentrations tended to increase with the age of the deck and decreased with the distance from the deck.

The same trends of leaching were also observed in the USA, where CCA is used as type C (Wu et al., 2004). It was also observed that chromium presented the greatest leachable concentrations for the wood that contain lower percentage of CCA chemical.

2.2.4 Waste management of CCA-treated wood

CCA is internationally registered as a class 1 red label chemical[1] and therefore has a restricted end use. However, the big volume of the waste wood sometimes mixed with CCA treated wood after its normal use, serves as a source of fuel to many poor people living in the peri-urban areas as they lack the access to alternative fuel (Goven, 2007).

There are various categorisations of CCA-treated wood. It is useful when countries use the same categorisation because it better allows a comparison on management practices. Australians rank number three in the world on the basis of per capita consumption of treated timber, behind New Zealand and the USA (Greaves, 2005; Mayes, 2008). When CCA-treated wood is burnt, Arsenic volatilises more than other elements and remains in the atmosphere as particulate matter, which is dangerous to human health and the environment as well (Solo-Gabrielle *et al.*, 2004).

[1] Class 1 red label chemical: must be preheated to burn

Waste minimization and disposal-end management are the options to minimize the impacts of CCA-treated wood during disposal. Disposal-end management should focus on improved sorting practices at construction and demolition recycling facilities and proper practices for disposing CCA-treated wood (Solo-Gabrielle & Townsend, 1998). Researchers reported that when waste wood, especially CCA treated wood is burned without specific controlled conditions, the metals enter the atmosphere in the form of small particles or particulate matter(PM) which have worse effects on both environment and human life (Kakitani et al., 2004)

For the side of the disposal sector, the efforts to deal with the problems associated with CCA-treated wood are at two levels: Source Reduction and Efficient management of CCA-treated wood waste.

The management options can broadly be classified as:

- Recycling; which implies the extraction of CCA metals by chemical, biological and electrodialytic methods (Wasson et al., 2005)
- Treatment and Destruction (Wu et al., 2006; Helsen et al., 1998); which implies wood liquefaction and thermal destruction.

The first step for the safe disposal of CCA-treated wood waste by thermal processes is considered to be the adoption of optimal thermal technology.

Amongst the various thermal processes available are incineration, pyrolysis and gasification (Figure 2-4). Each has an optimal set of operating conditions (temperature, treatment time, fuel/air ratio etc.) to minimize emissions of hazardous substances such as arsenic. These are further described below.

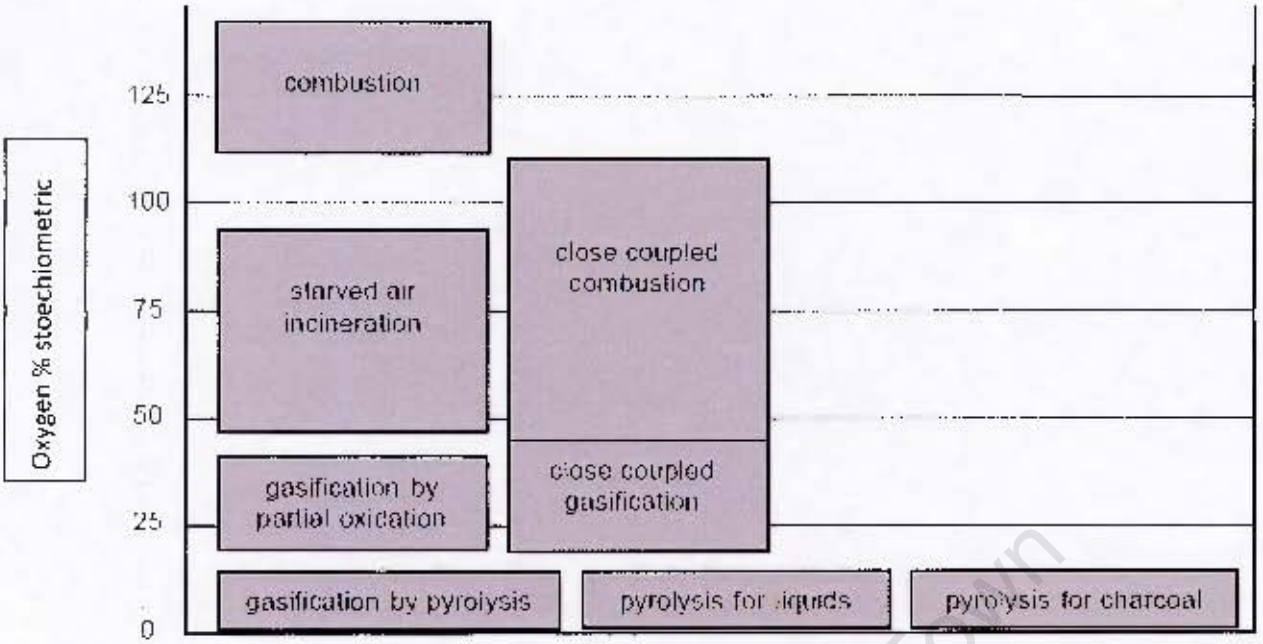

Figure 2-4: Oxygen requirements for each of the thermal processes

(Helsen and Van den Bulck, 2005; Wu et al., 2006)

1) Incineration

Incineration is often regarded as the simplest technique for the treatment of CCA-treated wood waste.

Advantages

• Easy to replicate and hence can be used at industrial level with minor retrofitting of boilers and air pollution control devices;

• Can be coupled with other industrial processes (such as production of cement, coal or steel) without the need for separate combustion boilers;

• Can be coupled to a recycling process by using extensive gas cleaning system to control air emissions. For instance, the arsenic collected by wet scrubbers can be recycled to the CCA solution production unit and the ash containing arsenic, copper and chromium can be processed in a copper smelter or recycled through chemical or electrochemical processes (Kristensen, 2002).

Disadvantages

• Extensive gas cleaning equipment required;

• The arsenic trioxide dust collected in filters poses problems for workers, hence from that point of view, wet methods are preferred;

• Unlike gasification and pyrolysis, no secondary fuels are produced and the energy generated has to be used instantaneously.

Hence, incineration can be an option for the disposal of CCA treated wood waste or mixed wood waste.

2) Co-incineration

This involves simultaneous or sequential combustion of two or more fuels. This technique is very popular in some industries, especially in cement kilns, where waste tires are burnt along with coal.

Advantages

- It is more economical as co-incineration can also be carried out in huge power plants and not just in incinerators;
- Since CCA wood will be a secondary fuel, its constant supply is not an issue as in the case of incineration of CCA wood alone;
- Mixing of fuels can compensate for the low heating value of CCA wood waste; also, the components of the other fuel (municipal waste, coal, etc.) may scavenge the CCA metals;
- It is easier to comply with concentration-based emission regulation due to the dilution in concentration of the CCA metals in the emitted air and in the ash but also consider the total released load (Wu et al., 2006)

Disadvantages

- The total emission may still be high, even though the concentration of CCA metals may be lower;
- Regulations may prohibit mixing of wastes;
- The lower concentration of arsenic in flue gas may make its removal more challenging;

According to Helsen and Van den Bulck (2005), in spite of these drawbacks, co-incineration seems to be the best available short term solution for thermal treatment of wood waste.

3) Pyrolysis

Pyrolysis is the chemical decomposition of organic materials by heating in the absence of oxygen and any other reagents. Pyrolysis done in the absence of moisture at very low residence times (< 2 sec) and high heating rates is called flash/fast pyrolysis. Flash pyrolysis can be used for production of pyrolysis oil, which can be used as a secondary fuel. Kakitani et al. (2004) assume that there are two types of arsenic release reaction during pyrolysis:

(a) The first possible pathway is due to the reacted arsenic compound, $CrAsO_4$, which appears to be released at around 400–500 °C, (eqs 1, 2 and 3)

$$4CrAsO_4 \cdot 6H_2O \leftrightarrow 24H_2O + 2CrO_3 + 2As_2O_5 \quad (1)$$

$$2As_2O_5 \leftrightarrow 2As_2O_3 + O_2 \quad (2)$$

$$2As_2O_3 \leftrightarrow As_4O_6 \quad (3)$$

(b) The second possible pathway is due to the unreacted arsenic compound, As_2O_5, in CCA-treated wood and occurs at much lower temperature, possibly 200 °C (eqs 4 and 5) (Kakitani et al., 2004; Mayes, 2008).

$2As_2O_5 \leftrightarrow 2As_2O_3 + 2O_2$ ..... (4)

$2As_2O_3 \leftrightarrow As_4O_6$ ..... (5)

Advantages

• Arsenic volatilization is lower than in incineration and gasification due to lower temperatures.

Disadvantages

• Arsenic volatilization is still non-zero as arsenic is highly volatile even at temperatures below 200 °C, (Kakitani et al., 2004; Wu et al., 2004; Wu et al., 2006; Rogers et al., 2007);

• Leaching of CCA metals is possible from the residue if it is disposed.

4) Gasification

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, petroleum coke or biomass, into carbon monoxide and hydrogen. It is a three step process, starting with pyrolysis (de-volatilization of the carbonaceous fuels), followed by the combustion of both volatiles and of the remaining char to form carbon dioxide and carbon monoxide, which provides heat for the subsequent gasification reactions. The first two steps occur very rapidly. In the third step, gasification occurs as the char reacts with carbon dioxide and steam to produce the syn gas (H_2 + CO, diluted with CO_2 + H_2O + N_2) which can be converted more efficiently to energy than wood. However, it is yet to be proven in practical systems or pilot scale studies for waste timber treatment (Helsen and Van den Bulck, 2005).

Advantages

• Syngas can be used as a fuel and has much higher energy efficiency as compared to wood;

• Since the process uses a limited amount of oxygen, less gas clean up is required as compared to incineration;

• High temperatures may result in the formation of metallic arsenic (potential reduction by CO), which is much easier to capture than arsenic trioxide as it has a higher sublimation temperature and doesn't go through a liquid phase upon cooling (Helsen and Van den Bulck, 2005).

Disadvantages

- Very efficient air pollution control devices are required to capture all of the arsenic released during gasification;
- In order to capture arsenic trioxide at such high temperatures, it is required to have all the arsenic released in metallic form, which is mostly not possible;
- The high temperature and fine particle size requirement make it an expensive technique.

An extensive review of available thermochemical conversion processes for disposal of CCA-treated wood waste by Helsen and Van den Bulck (2005) suggests that co-incineration may be the best short-term solution for disposal (Wu et al., 2006).

It is practically impossible to have no hazardous emissions from the thermal treatment of CCA-treated wood waste; hence, efforts are made to capture all of the arsenic generated. Various air pollution control devices are used by industries to control air emissions. It is important to keep in mind that the available pollution control devices in the industry still have to propose a technology which can be effectively utilized (Wu et al., 2006).

2.2.5 Phase down of CCA treated wood in USA

The American Wood Preservers' Association (AWPA) specified three formulations for CCA. There are CCA type A, B and C. The differences of the A, B and C types were in the relative proportions (oxide basis) of chromium, copper, and arsenic. CCA-C is the preferred choice for CCA treatment of wood as it offers the best combination of performance and leach resistance. The amount of CCA chemical added to wood depends upon the intended use of the treated wood product. Wood used for above ground applications is treated in the U.S. using a minimum of 4 kg of chemical per cubic meter of wood product (kg/m^3). Utility poles are treated at 6.4 kg/m^3 and wood used for pilings within marine environments is treated at 40 kg/m^3.

CCA was the most common wood treatment preservative utilized in the U.S. during the 1980s, 1990s, and early 2000's. Due to the predominance of CCA-treated wood until recent times, the majority of outdoor wood structures currently in-service in the U.S. are treated with CCA and these structures will ultimately require disposal long into the future. Thus, the impacts from CCA-treated wood will likely be experienced during in-service use and during disposal for many years to come (Solo-Gabrielle et al., 2004). For example, in Florida, in 1996, the majority of the CCA-treated waste

processed through construction and demolition recycling facilities, resulted in a wood waste composition containing on average 6% CCA-treated wood (Wu et al., 2004). There was a remarkable increase in CCA treated wood volume from 1970 to 1996. In 1970, the total volume of treated wood products was 248 million cubic feet of which 39 million cubic feet were treated with CCA. By 1996, this figure increased to 591 million cubic feet for all products and 467 million cubic feet for CCA-treated products. However, the primary market for wood waste is energy recovery and, therefore the majority of CCA-treated wood waste is burned for energy recovery purposes (Wu et al., 2004; Wu et al., 2006; Solo-Gabrielle & Townsend, 1998).

Solo-Gabrielle at al. (2002) reported that when CCA-treated wood represents 5% or more of a recycled wood mixture, the ash from its combustion will typically be characterized as a TC (Toxicity Characteristic) hazardous waste. The USA and the Canadian wood preservation industries in conjunction with the US EPA and the Canadian Pest Management Regulatory Agency (PMRA) agreed on a voluntary transition away from CCA-treated wood products for non-industrial usage. This transition took effect from January 2004 (Greaves, 2005).

2.2.6 Ways to minimize CCA treatment

The minimization of CCA treatment should focus on the use of alternative wood treatment preservatives that do not contain arsenic so that after the normal use, the wood can be burnt without posing health or environmental risks. Emphasis should be laid on preventing overuse of preserved wood and minimization of wood waste during construction (Wu et al., 2006). Non-arsenical chemicals include Acid Copper Chromium (ACC), Alkaline (Ammoniacal) Copper Quaternary (ACQ), Copper Boron Azole (CBA), Copper citrate (CC), copper diethyldithiocarbamate (CDDC), chromated zinc chloride (CZC), copper naphthenate, copper-8-quinolinolate (Cu-8-Q), sodium fluoride, and zinc naphthenate, etc. (Solo-Gabrielle et al., 2004; Read, 2003; Khan et al., 2004).

Breedt (2010) reported that to date there are only three preservative treatment plants in South Africa that can produce timber treated with Tanalith E™, which is arsenic free, but do so for export purposes only. The alternatives are effective, and somewhat more expensive, but they may be used instead of CCA in many applications if the consumer so desires, (Greaves, 2005). Only ACQ and Copper Azole are the CCA alternatives used in South Africa. Efforts are also being made to substitute CCA treated wood by other materials (untreated cedar, teak, etc) (Wu et al., 2006).

2.3 Occurrence and toxicity of the metals under investigation

The metals considered in this investigation are arsenic, chromium and copper.

Effects associated with CCA-treated wood exposure may differ from effects caused by exposure to each component in isolation (Read, 2003), which are presented in the following sections.

2.3.1 Arsenic

2.3.1.1 Occurrence and exposure

Arsenic is a naturally occurring element. Generally it is found at higher concentrations in sedimentary rocks than in other rock types, and it is also commonly associated with sulphide deposits in the mineral form Arsenopyrite: FeAsS. Major anthropogenic sources of arsenic in the environment include smelting operations and a variety of pesticides used in pressure treating wood for construction purposes. When CCA is used as a wood preservative, arsenic has the potential to leach out of the wood over time. When such wood waste it is disposed in a landfill, arsenic migrates and is leached out possibly (resulting) in groundwater contamination (Khan et al., 2004).

Arsenic is released into the air when the wood is burnt (Khan et al., 2004). It should be noted that the volatility point of arsenic has been difficult to specify, due to the different states of arsenic and to the presence or absence of unreacted compounds. After long-term weathering, CCA-treated wood waste may contain only a small amount of unreacted arsenic compound, because the free arsenic compounds may have already been washed or leached out of the treated wood (Kakitani et al., 2004). Rogers et al. (2007) reported some arsenic volatilisation at lower combustion temperatures. The implication appeared to be that all thermal treatments give rise to some level of arsenic volatilisation (Figure 2-5).

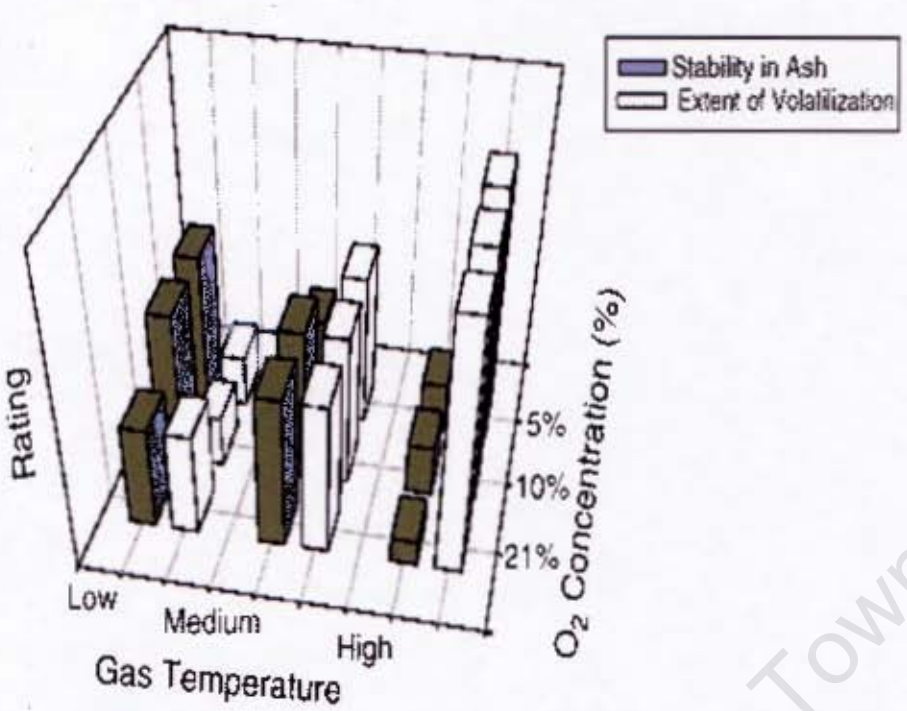

Figure 2-5: Stability and volatilization of arsenic during combustion

(Rogers et al., 2007)

2.3.1.2 Toxicity

The environmental consequences of arsenic volatilisation are linked to the mechanism by which the arsenic condenses to form particles in the waste gas. From a human health perspective, particles below 1 μm in diameter are considered especially dangerous, due to their ability to penetrate deeply into the lungs. Therefore the size of particles in which arsenic is found is particularly important. While no studies have as yet been conducted on treated timber combustion, to determine the mechanism of arsenic condensation, research in coal combustion has shown that arsenic tends to be concentrated in the submicron range of entrained particles found in the waste gas. Therefore, combustion technologies for CCA-treated timber have to develop a method to remove entrained particles from the waste gas without compromising the environment (Wu et al., 2006).

Jain & Ali (2000) and Hinkley (2003) reported the existence of two types of arsenic toxicity; acute and chronic toxicity. Arsenic is known as a class A human carcinogen[2] (Hinkley, 2003). Biologically,

[2] class A carcinogen is described as pollutant with adequate human data indicating the chemical causes cancer in people.

trivalent arsenic is about 60 times more toxic than when it is in its oxidized pentavalent state, the conversion of which occurs during combustion (Khan et al., 2004). It is also said that inorganic arsenic is more toxic than organic arsenic, as emerging medical studies indicated that inorganic arsenic is not only a potent human carcinogen itself, but also that even very small arsenic exposure can cause existing tumors to grow more rapidly and aggressively (Maas et al., 2004).

1) ACUTE TOXICITY

The ingestion of arsenic causes generally the acute poisoning which requires immediate medical attention. The first manifestation of acute poisoning includes burning and dryness of the mouth and throat, dysphasia, abnormal pain, projectile vomiting, profuse diarrhoea, hematuria, muscular cramps, facial oedema and cardiac abnormalities, and due to dehydration, shock can develop quickly (Jain & Ali, 2000). Skin and eye contact can cause irritation and burning. Arsine gas (AsH_3), formed under strongly reducing conditions, is lethal to humans even at low doses between 25 and 50 ppm in air (Wu et al., 2006).

2) CHRONIC TOXICITY

While arsenic exposure can occur from food, air and water, all major chronic arsenic poisonings have stemmed from water and air, and those are usually the predominant exposure routes. Exposure to arsenic leads to an accumulation of arsenic in tissues such as skin, hair and nails, resulting in various clinical symptoms such as hyperpigmentation and keratosis (Jain & Ali, 2000; Kapaj et al., 2006).

In a study with mice, it was found that chronic low-level As exposure may affect heme metabolism, causing porphyrin changes. These changes may appear in the beginning stages of arsenicosis, before the carcinogenesis and can be a clinical indicator to diagnosis (Kapaj et al., 2006).

Continued low dose exposure over a long period of time leads to chronic toxicity and symptoms of poisoning start to manifest. The biological systems affected include the respiratory, gastro-intestinal, cardio-vascular, nervous and haematopoietic systems. Poisoning causes the loss of appetite, nausea and some vomiting, dry throat, shooting pains, diarrhoea, nervous weakness, tingling of the hands and feet, jaundice and erythema. There is also an increased risk of skin, internal organ, liver, bladder and lung cancers (Jain & Ali, 2000; Kapaj et al., 2006; Wu et al., 2006).

2.3.1.3 Arsenic guidelines in drinking water

Several countries have tightened arsenic guidelines in drinking water, with Canada decreasing the maximum allowable level from 50 to 25 μg/L and the U.S. from 50 to 10 μg/L. In 2006, Canada tried to contemplate a further decrease to 5 μg/L. The reason for these regulatory changes was the realization that arsenic can still cause deleterious effects at lower concentrations than was previously thought (Kapaj et al., 2006). According to WHO and the US EPA, 10 μg/L should be the permissible concentration of arsenic in drinking water. This is slightly higher than the proposed Canadian and Australian concentrations of 5 and 7 μg As/L, respectively (Kapaj et al., 2006).

2.3.2 Chromium

2.3.2.1 Occurrence and exposure

Chromium exists in small quantities throughout the environment. The most important commercial ore is Chromite ore ($FeCr_2O_4$). Hexavalent chromium compounds are used in the manufacture of pigments, metal finishing and chromium plating, stainless steel production, hide tanning, as corrosion inhibitors, and wood preservation. Occupational exposure to chromium (VI) generally occurs by inhalation and dermal contact. However, when a substance is inhaled, a small amount is inevitably ingested (Clu-in Contaminants, 2010).

It is not easy to classify release in terms of trivalent or hexavalent chromium. A number of combined activities account for a large amount of the chromium in the atmosphere; those activities include combustion activities at utilities, fugitive emissions from road dust, and formerly industrial cooling towers. In general, most chromium in ground water bodies is found in the +3 valence state. However, hexavalent chromium anions will be the predominant form of dissolved chromium. Chromium enters the air, water, and soil mostly in the chromium (III) and chromium (VI) forms. In air, chromium compounds are present mostly as fine dust particles which eventually settle over land and water.

2.3.2.2 Toxicity

While chromium (III) is an essential nutrient that helps the body use sugar, protein, and fat, Chromium (VI) is almost 100 times more toxic than Chromium (III) (Ballar, 1998). Breathing high

levels of chromium (VI) can cause irritation to the nasal passages resulting in a runny nose, nosebleeds, ulcers and holes in the nasal septum. However, there is not much chromium volatilization from combustion of CCA-treated timber, even at high temperatures (Figure 2-6), although elevated oxygen concentrations do result in higher airborne chromium, presumably through an enhanced oxidation mechanism (Rogers *et al.*, 2007). It has been reported that at a concentration of 0.008 $\mu g/m^3$ there would be a one-in-ten-thousand risk of developing cancer during one's lifetime (IRIS, 1999).

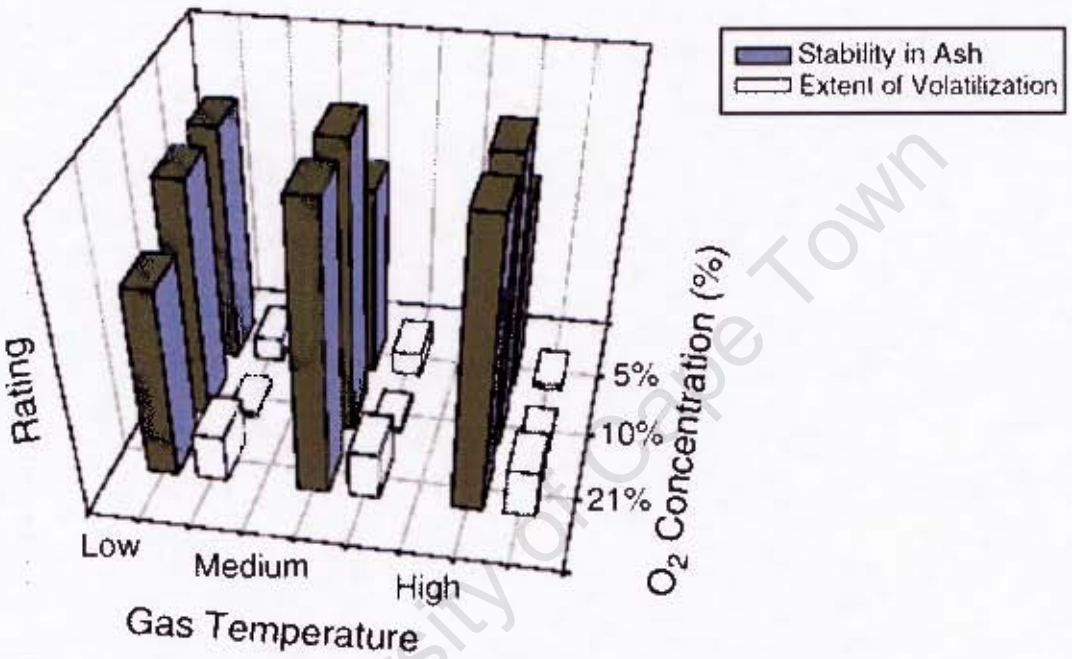

Figure 2-6: Stability and volatilization of chromium during combustion

(Rogers et al., 2007)

Ingestion of large amounts of chromium (VI) may cause stomach upsets, ulcers, convulsions, kidney and liver damage and even death. Read (2003) reported that hepatic, gastrointestinal and renal effects are the most common following ingestion and have been reported in individuals who ingested between 4-29 mg/kg of body weight of hexavalent chromium, which resulted in death in all cases. The estimated lethal dose for children is 10 mg/kg of body weight.

Some people have extreme dermal sensitivity to chromium (VI) or chromium (III). The main reason why Cr (VI) is so toxic, is that one of the reduction products of Cr (VI) is Cr (V). Allergic reactions, consisting of rigorous reddishness and inflammation of the skin, have been noted, the reduction of Cr (VI) occurs due to the action of acidity + enzymes within the body, while dermal contact with

certain chromium (VI) compounds can cause skin ulcers. As Cr (VI) as is a large molecule, it often passes out of the body.

During the passage out, Cr (VI) will continue to oxidize anything it can find on its way, leaving deposits of the moderately safe Cr (III) and absolutely unsafe Cr (V) behind. However, it can lodge in the body in the fine capillaries in the kidneys, intestines or lungs and act as carcinogen.

Several research studies have shown that a number of chromium (VI) compounds can increase the risk of lung cancer. Animal studies have also shown an increased risk of cancer. The WHO, the US Department of Health and Human Services (DHHS) and the US EPA have determined that chromium (VI) and its compounds cause cancer in humans (IRIS, 1999).

2.3.3 Copper

2.3.3.1 Occurrence and exposure

Copper is a pliable, malleable transitional metal, with a bright reddish metallic gleam, and also an excellent conductor of both heat and electricity. Copper occurs naturally in a wide range of mineral deposits. It is used to make textiles, marine paints, electrical conductors and wires, plumbing fixtures and pipes, as well as coins and cooking utensils. As copper is very toxic to fungi and algae, it is also widely used as a wood preservative and fungicide.

In the survey done by the Ontario Ministry of Environment (MOE), it was demonstrated that copper is an essential micro-nutrient required in the growth of both animals and plants. In plants, it is especially important in seed production, disease resistance and regulation of water. In humans, copper helps in the production of blood haemoglobin (MOE, 2001).

2.3.3.2 Toxicity

MOE reported that both humans and animals need some amounts of copper in their diets, but exceedingly high concentrations of copper can be toxic. The most common warning sign of copper toxicity is the damage to red blood cells, lungs, as well as the liver and pancreas (MOE, 2001). In a study conducted by Rogers et al. (2007), no effect from copper inhalation was found due to the

fact that copper does not volatilise easily (figure 2- 7). Its toxicity is mainly associated with ingestion.

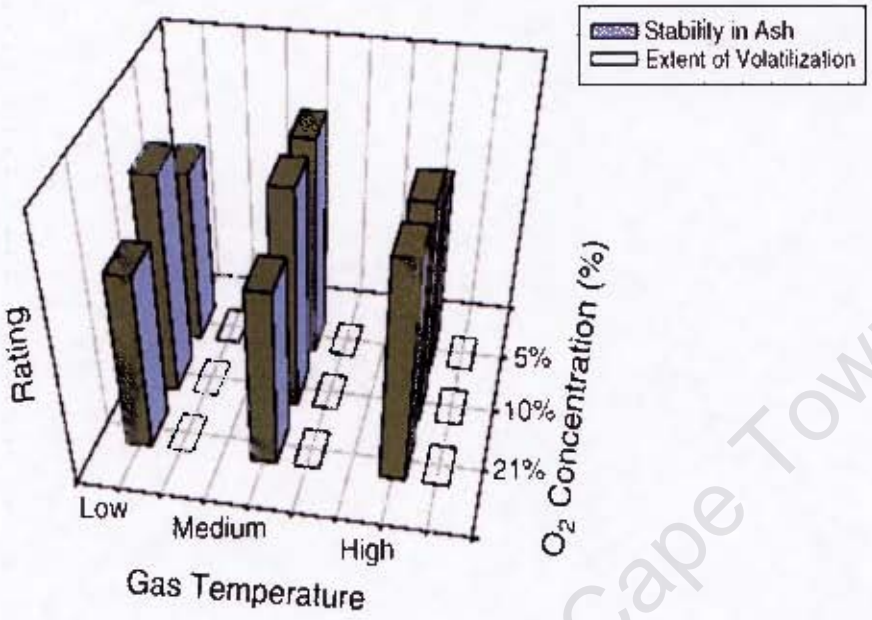

Figure 2-7: Stability of copper during Combustion

(Rogers et al., 2007)

2.4 Air pollution

The official definition of air pollution in South African law, is any change in the environment caused by any substance emitted into the atmosphere from any activity, where that change has an adverse effect on human health or well-being or on the composition, resilience and productivity of natural or managed ecosystems, or on materials useful to people, or will have such an effect in the future (City of Cape Town, 2007).

The normal clean air is composed of nitrogen (78.1%), oxygen (20.9%), carbon dioxide (0.03%), noble gases such as argon (0.9%) and water vapour, as well as particulates (dust, ash, sand and pollen).

Polluted air, however, contains quantities of gases and particulates that can harm animals and plants, interfere with natural ecosystem, reduce the service life of materials through corrosion (e.g. metals).

Pollutants derive from natural as well as anthropogenic sources. Any activities that involve combustion (heating and burning) create air pollutants. These activities include:

- Combustion of gasoline by motor vehicles
- Coal combustion for electricity generation
- Waste disposal through incineration
- Domestic activities such as cooking and heating using electricity, coal, paraffin, wood or gas
- mining
- Forest and grass fires

Volcanoes and pollen are also sources of pollution.

2.4.1 Health effects

By the nature and size of the pollutants particulate matter (PM) are fine particles made up of tiny solids or liquid droplets that are so small that they can get deep into the lungs and cause serious health problems. Air quality protection regulations concentrate on particles that are 10 micrometres in diameter or smaller, because those are the particles that generally pass through the throat and nose and enter the lungs.

Epidemiologic studies have demonstrated an association between exposure to particulate matter and adverse human health effects at concentrations commonly found in urban areas around the world (Karthikeyan et al., 2006).

Particulate matter from dust, wood burning and diesel was reported by the City of Cape Town to be the greatest air pollutant in Cape Town, especially in winter (City of Cape Town, 2007). In their Newsletter no 38, WHO believes that a reduction in the levels of one particular pollutant, namely PM_{10} (aerosol with less than 10 micrometer in diameter), could reduce deaths by as much as 15% in polluted cities around the world every year (WHO, 2006).

Numerous scientific studies have linked particle pollution exposure to a variety of problems, including:

- Severe respiratory symptoms, such as irritation of the airways, coughing, or difficulty breathing as a result of decreased lung function; aggravated asthma; development of chronic bronchitis and tuberculosis (Guha Mazumder, 2003; Kapaj et al,. 2006)
- irregular heartbeat;

- nonfatal heart attacks; and
- Premature death in people with heart or lung disease, especially children.

It was reported by the City of Cape Town (2007) that people with heart or lung diseases, children and the elderly are the most likely to be affected by particle pollution exposure.

It was reported from the fact sheet of Fine Particle Pollution Program (FP^3) (the program that advises Northeast Ohio residents when fine particle pollution (soot) reaches unhealthy levels) that a 24-hour average of 40 micrograms per cubic meter (40 $\mu g/m^3$) of fine particles is considered "Unhealthy for Sensitive Groups" and a 24-hour average of 65 $\mu g/m^3$ is determined "Unhealthy" for the entire population, (FP^3, 2006)

2.4.2 Environmental effects of air pollution

2.4.2.1 Visibility reduction and haze

Haze is caused when sunlight encounters tiny pollution particles in the air. Some light is absorbed by particles. Other light is scattered away before it reaches an observer. More pollutants mean more absorption and scattering of light, which reduce the clarity and colour of what we see. Some types of particles such as sulphates scatter more light, particularly during humid conditions. Particulate matter pollution is the major cause of reduced visibility (haze). This brown haze is also reported by City of Cape Town (2007) to be a result of particulate matter emission from both vehicles and fuel combustion.

Some haze-causing particles are directly emitted to the air. Others are formed when gases emitted to the air form particles as they are carried a long distance from the source of the pollutants (U.S. EPA, 2010).

2.4.2.2 Environmental damage

Particles can be carried over long distances by wind and then settle on ground or water. The effects of this settling include; depending on the nature of the particles making lakes and streams acidic; changing the nutrient balance in coastal waters and large river basins; depleting the nutrients in soil;

damaging sensitive forests and farm crops; and affecting the diversity of ecosystems (U.S. EPA, 2010).

Particulate matter is one of the six criteria pollutants according to U.S. EPA (Chong et al., 2002; City of Cape Town, 2007; Von Blottnitz et al., 2007).

2.4.3 Arsenic in Tobacco smoke

Tobacco smoke is a major recognised source of As in air. It is interesting to note that mainstream cigarette smoke contains 0.04 to 0.12 μg As per cigarette (Kapaj et al., 2006).
It is already known that cigarette smoking is a main risk factor for lung cancer and the authors found that cigarette smoking plus ingestion of As from drinking water had a synergistic effect, thus increasing the risk of lung cancer. Kapaj et al. (2006) suggested that reduction in As exposure should reduce the lung cancer risk in cigarette smokers.

2.5 Particulate matter and CCA composition

The size of particles is directly linked to their potential for causing health problems. A possible pathway for exposure through air-particulates is the incidental use of preserved wood (CCA-Treated wood in our study) in open fires, indoors or outdoors (Kapaj et al., 2006). The content of As in air-particulates from open fires where CCA-treated wood was used, was found to exceed the German air quality standards by a 100-fold (Kapaj et al., 2006). It was reported by Benson (2007) that a number of metal compounds including Chromium, Copper and Arsenic are among the composition of particulate matter.

Arsenic in particulate matter poses a great threat to human health. In the second edition of the Air Quality Guidelines for Europe, published by the World Health Organization (WHO) in 2000, it was reported that there is no safe amount when inhaled (Fang et al., 2011). From this, it can be confirmed that some of the effects of particulate matter are associated with the presence of the metals mentioned above.

2.5.1 Particulate matter and Air Quality Guidelines

EPA groups particle pollution into two categories:

1) Source of PM_{10}

"Inhalable rough particles," such as those found near roadways and dusty industries, are smaller than 10 micrometers and sometimes greater than 2.5 micrometers in diameter. They are mechanically produced by the fall to pieces of larger solid particles. Further these particles can be produced by road traffic through air turbulence that can stir up dust as well as sea (WHO, 2003)

2) Source of $PM_{2.5}$

"Fine particles," such as those found in smoke and haze, are 2.5 micrometers in diameter and smaller. These particles can be directly emitted from sources such as forest fires, or they can form when gases emitted from power plants, industries where combustion and automobiles react in the air. It is in this category where heavy metals investigated in this study are found.

It has been found that many kinds of combustion particles from power plants and residential heating (residual oil fly ash, coal fly ash, wood heating particles and transport/traffic-related particles) induce toxic responses after exposure of animals and humans. In addition, particles released to air from different kinds of factories have been found to be toxic (WHO, 2003).Those particles mainly include toxic organic compounds and heavy metals (Air Info Now, 2010).

Based on known health effects, both short-term (24-hour) and long-term (annual mean) guidelines are needed for both indicators of PM pollution. An annual average of 10 $\mu g/m^3$ ($PM_{2.5}$) was considered as the lower end to which significant effect were observed in American Cancer Society's study, (WHO, 2005)

$PM_{2.5}$: 10 $\mu g/m^3$ annual mean

25 $\mu g/m^3$ 24-hour mean

PM_{10}: 20 $\mu g/m^3$ annual mean

50 $\mu g/m^3$ 24-hour mean (Source: WHO, 2005)

2.5.2 Arsenic guidelines in air

ARSLAND report in (2006) stated that when 'arsenic' is used in the context of airborne particulate matter it refers to inorganic arsenic. Concentrations of arsenic in ambient air range from 1 – 3 ng/m^3 in rural areas to around 20 – 30 ng/m^3 in urban areas. Annual mean airborne arsenic concentrations

in the UK have been stated to be 'typically in the region of 1 – 2 ng/m^{3}' with a highest value of 8.36 ng/m^{3} (Maggs, 2001).
Across Europe, values are 0.2 – 1.5 ng/m^{3} (rural), 0.5 – 3 ng/m^{3} (urban background and traffic-related sites) and 50 ng/m^{3} (industrial sites) (ARSLAND, 2006).

Whatever quantities of arsenic in the air, the impact on health depends very much on the particulate size distribution, with PM_{10} arsenic being the accepted metric for the assessment of health effects due to the inhalation of airborne particulate matter.

Arsenic and arsenic compounds were evaluated by the International Agency for Research on Cancer (IARC) and evidence was found that these compounds are carcinogenic to humans, (EHC 224, 2001). Lung cancer is considered to be the critical effect of airborne arsenic inhalation and a lifetime risk of 1.5 x 10^{-3} is estimated for exposure to 1 µg/m^{3} airborne arsenic. From this it can be estimated that the excess lifetime risk level is 1:10 000, 1:100 000 and 1:1 000 000 at air concentrations of 66 ng/m^{3}, 6.6 ng/m^{3} and 0.66 ng/m^{3} respectively (WHO, 2000; EHC 224, 2001; ARSLAND, 2006). It is thought that 0.66 ng/m^{3} (one-in-a million risk) overestimates the 'true risk' (EHC 224, 2001).

The regulations on airborne arsenic in the European Community were introduced because of evidence that arsenic '...is a human genotoxic carcinogen and that there is no identifiable threshold below which the substance does not pose a risk to human health' (ARSLAND, 2006; Fang, 2011).
The European Community state that, from a cost effectiveness point of view, ambient arsenic air concentrations cannot be reduced to a level which will not pose a significant risk to human health, and that target values need to be identified which would not require any measures entailing disproportionate costs, but which would require all Member States to take all cost-effective measures.

The Directive of the European Community had set a target value of 6 ng/m^{3} for an annual average, total PM10 arsenic concentration to be met by 2010 (ARSLAND, 2006).
According to the regulatory limit (Table 2-3) by the Occupational Safety and Health Administration (OSHA), arsenic should not exceed 10 µg/m^{3} in a work place for 8 hrs (Wu et al., 2006).

Table 2-3: Standards and Regulations for inorganic arsenic

(Wu et al., 2006)

Agency	Focus	Level	Comments
Governmental Industrial Hygienists	Air: Workplace	10 μg/m^3	Advisory; TLV/TWA
National Institute for Occupational Safety and Health	Air: Workplace	2 μg/m^3	Advisory; 15 minute ceiling limit
Occupational Safety and Health Administration	Air: Workplace	10 μg/ m^3	Regulation; PEL over 8-hour day
TLV/TWA (threshold limit value/time-weighted average): time weighted average concentration for a normal 8-hour workday or 40-hour workweek to which nearly all workers may be repeatedly exposed. PEL (permissible exposure limit): highest level averaged, over an 8-hour workday, to which a worker may be exposed.			

2.6 Methods employed

2.6.1 Methods employed to investigate the concentrations of chromium, copper and arsenic from CCA treated wood

Different methods can be used to determine the concentration levels of different constituents in wood and other plants. Rodushkin *et al.* (1999) in their article "comparison of two digestion methods for elemental determinations in plant material by ICP techniques" recommended the following techniques for digesting wood and other plant materials:

1. Open vessel

The open vessel method required 2 g of the sample and 10 ml of HNO_3 (analytical grade) for 30 min. The mix is put into an aluminium block, and the temperature is elevated to 120 ^{0}C for 2 h. 100 ml of water is added and the mix is left to cool at room temperature. A 10 ml (aliquot) is taken to be centrifuged at 4000 rpm for 5 min before ICP/AES analysis is done.

2. Microwave digestion

This article reports that this method requires 0.5 g of the sample into a PFA digestion vessel, 5 ml of nitric acid (additionally purified) and 0.5 ml of hydrogen peroxide. The mix is put into the microwave oven and digested at 600 W power for 1 h. The vessel is removed and cooled at room temperature. The digest is transferred to a plastic auto sampler tube and diluted with water to 10 ml then mixed, centrifuged at 4000 rpm for 5 min and diluted further five-fold for ICP/AES analysis.

Conclusion: results obtained indicate that both procedures possess qualities that make them suitable for ICP/AES determination of major, minor, and trace elements.

As the use of reagents like perchloric, hydrofluoric and sulphuric acids is avoided, extended supervision during sample preparation is unnecessary and side effects are minimized (Rodushkin et al,. 1999).

Microwave digestion is recommended if high analyte recovery is of great importance. The only advantage of procedure 1 is its low equipment cost and less demanding sample preparation.

Stilwell et al. (2003) developed a procedure to determine the amount of Cr, Cu and As in wipe samples based on acid extraction using nitric acid. The test material used for method development was CCA wood powder from sawdust mixture obtained during CCA wood cutting. Different percentages of nitric acid were used and they came up by adopting an extraction in 10% HNO_3 at 65°C for 2 h as standard procedure. Their study also reported that the concentrations of Cr, Cu and As in the CCA wood powder were determined in six replicates by microwave-assisted nitric acid extraction (EPA method 3051) followed by analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

The results thus obtained by Stilwell et al. (2003) of 2714±62, 1557±44 and 2654±26 mg/kg of Cr, Cu and As were in reasonable agreement with the nominal values of 3120, 1840 and 2800 mg/kg of Cr, Cu and As as expected in the CCA-treated wood sample, respectively.

2.6.2 Methods employed to investigate Arsenic in air

1) Acetic acid and ethanol

Rogers *et al.* (2007) investigated the volatilization of Arsenic when CCA treated wood is burned. They passed the wood samples through a non-porous ceramic furnace and the species volatilized during combustion of the sample was allowed to pass through a filter, while fly ash was collected on it. The filter was finally washed with dilute acetic acid and ethanol and the washings were analysed for dissolved metals by ICP-AES.

2) Nitric acid+ hydrogen peroxide+ perchloric acid and the addition of ethanol

In the study done by Giles (2005) on 'Sampling and Analytical Methods: Arsenic, Cadmium, Cobalt, Copper, Lead, and Nickel', they used a calibrated personal pump equipped with MCE (mixed-cellulose ester) membrane filter with back-up pad (BUP) contained in a polystyrene cassette to collect the air samples. The filters with specimen were digested in microwave oven with nitric acid and hydrogen peroxide, for 12 minutes at 104 °C followed by the addition of perchloric acid at 86 °C for 6 minutes. Ethanol was also added. After cooling, the digest was analysed by ICP/MS. This method is critical because of the digestion of filter cassettes, while those cassettes can be used for next sampling. The method is also very expensive and complicated as it used 5 different products for digesting the samples.

3) Nitric acid and perchloric acid

Alvarez *et al.* (2004) used a high volume sampler equipped with a cascade impactor PM_{10} inlet to collect air samples. The particle samples were analysed by acid digestion assisted by microwave heating using a HNO_3:$HClO_4$ (3:1, v/v) mixture. Thereafter, Arsenic was determined by hydride generation atomic absorption spectrometry (AAS). This method is not suitable since the use of $HClO_4$ may cause explosion when organic compounds are present in the samples.

4) Aerosol sample collection with a MinVol portable air sampler and analysed by nitric acid, hydrofluoric acid and hydrogen peroxide

In Singapore, Karthikeyan et al. (2006) used a MinVol portable sampler for PM collection over 24 hours at 5 L/min. Different filter substrates i.e. Teflon, Zeflour and quartz were used to compare their efficiency. Different size fractions of atmospheric particulate matter including PM_{10}, were collected and weighed. The filters were weighed using a microbalance (6 decimals) before and after the collection so as to know the mass of collected particulates. The filters were handled carefully by

the stainless forceps to avoid any loose of particulate matter and were put into individual containers until extraction.

The mass concentration of PM_{10} were calculated from the amount of PM_{10} collected onto the filter [µg] divided by total volume of ambient air drawn through the filter [m^3].

After all calculations of the mass of PM_{10}, the filters were digested using HNO_3 (4 mL), H_2O_2 (2 mL) and HF (0.2 mL). In contrast to the Quartz filter, Teflon and Zeflour filters did not dissolve completely in the acid mixture.

Yong et al. (2000) and Karthikeyan et al. (2006) reported that the total digestion of the filter is not necessary for determining total metal since ICP has the capability to dissociate all forms of trace metals because of high energy and ionization provided by the plasma. ICP/MS was used to determine the total metal concentration in this study.

This extraction process was found to be simple, fast and reliable and can be used for analysing numerous air particulate (Karthikeyan et al., 2006).

Conclusion: All these methods have advantages and disadvantages and it is clear that in all the methods mentioned above, only the total arsenic was investigated. The digestion time is long. As informed above by Yong et al. (2000) and Karthikeyan et al. (2006), the only matters should be that all the collected samples should be digested even though the filter is not.

2.7 Concluding notes

The literature review highlighted the history of CCA treated wood and its longstanding application. It detailed the behaviour, dangers and toxicological effects of the elemental constituents of CCA. In many countries, research studies have been carried out on the characteristics, leaching and deportments and dislocation of chromium, copper and arsenic from CCA-treated wood. Possible toxicological effects to humans and environment were also reported when CCA-treated wood is burned. But controlled burnings can be a means of minimising pollutant emissions from CCA-treated wood. It was also seen that South African wood industries use CCA treatments for the wood used in the country, with little market penetration so far of alternative treatments, which mainly are done for export purposes. No published studies on CCA-treated wood waste management in South Africa were found.

3 Approach and Methods

This chapter outlines the experimental work to be carried out, in order to achieve the study's objectives. As stated in chapter 1, the main objective of this dissertation is to investigate whether informally operating urban caterers and their clients are exposed to any significant toxicity risk when CCA-treated wood is burned. The emphasis is put on investigating whether CCA-treated wood is being used by informal caterers, if so, what levels of CCA it contains, and how much are they exposed to the smoke when the CCA-treated wood is burned. Furthermore, by comparing the results of this study to the regulatory limits detailed in the literature, the researcher can determine whether these levels pose risks to the people.

3.1 Research motivation and research questions

In South Africa, wood fuel is predominantly used by people in low income groups living in poor conditions, for example in informal settlements, rural areas and townships. Caterers in those areas use wood as a fuel for cooking or *braaing* (grilling of meat) and some households use it for heating or cooking purposes. Wood industries in South Africa do process wood with CCA and classify it according to the levels and quantities of CCA impregnations thus used for different applications. This study limits its scope to wood used as fuel by informal caterers in the townships and informal settlements located in urban and peri-urban areas of Cape Town.

The objective of this dissertation will be achieved by answering the following research questions:

1. Is CCA-treated wood used by informal caterers?

This will be answered by collecting some treated wood samples from caterers' wood-stocks and ready to be used as fuel and analyse them.

2. Is there any release of significant pollutants into the environment from the use of CCA-treated wood as fuel?

This will be answered by analysing and calculating the levels of the CCA constituents in each wood sample, and the same analysis will be carried to smoke samples as well, which will be collected from close to the wood fire.

3. Is the concentration of the pollutants released harmful to the environment and human wellbeing?

This will be answered by comparing results that we find with available research already done and limits already set.

The following sections provide information as to where the samples were collected from, considering Cape Town International Airport as a reference (Section 3.2), the procedures used to collect both wood and air samples (Section 3.3) with specific attention given to the PM_{10} sampling and the instrument used to collect the smoke samples. The operating protocols, experimental approach and analytical techniques used are detailed in section 3.4 of this chapter.

3.2 Site descriptions

Sites at which informal caterers are working were selected in and around Cape Town so as to compare whether caterers operating in urban area and those in peri-urban area make use of the same type of fuel wood.

In the urban context, three townships i.e. Nyanga, Khayelitsha and Langa were chosen to represent urban areas. In an earlier exploratory study in Nyanga and Khayelitsha on ash left behind after use of wood as fuel, the results showed no significant levels of the suspected toxic in the wood treatments (Claasen & Sibanda, 2009). A site in Langa was added during the course of the investigation as a result of a collaborative study with colleagues from the Occupational Health unit of the Faculty of Medicine, who investigated human exposure. All three areas are situated in the municipal area of the City of Cape Town and are old townships. These three townships are situated not more than 20 km from Cape Town International Airport which allows them to be considered together.

In the peri-urban context, locations in Kayamandi (near Stellenbosch), Worcester and Mbekweni (near Paarl) were chosen for comparative purposes. These townships are situated at more than 30 km from Cape Town International Airport which allows them to be considered together as well.

3.2.1 The urban context

Nyanga

Nyanga is one of Cape Town's oldest and largest black townships. It was established in 1955. It lies about 26 km from the city centre along the N2, close to the Cape Town International Airport (Figure 3-1) and, like most of townships in the country, originated as a result of the migrant labour system. Nyanga is still poor and is made up mostly of informal settlements where people live in shacks (Wiechowsk & Bak, 2007). However, organizations opened businesses in Nyanga and many are still opening. Entrepreneurs have opened barber shops, hairdressing salons, tuck shops etc., and informal traders and fruit sellers line the main streets. The informally operating caterers include braaiers of meat, sausages and sheep head, chicken boilers, African beer brewers and maize vendors. Those are the main productive users of fuel wood; in addition there are those who use it in their homes for other purposes as heating, cooking (SA-Venues, 2011).

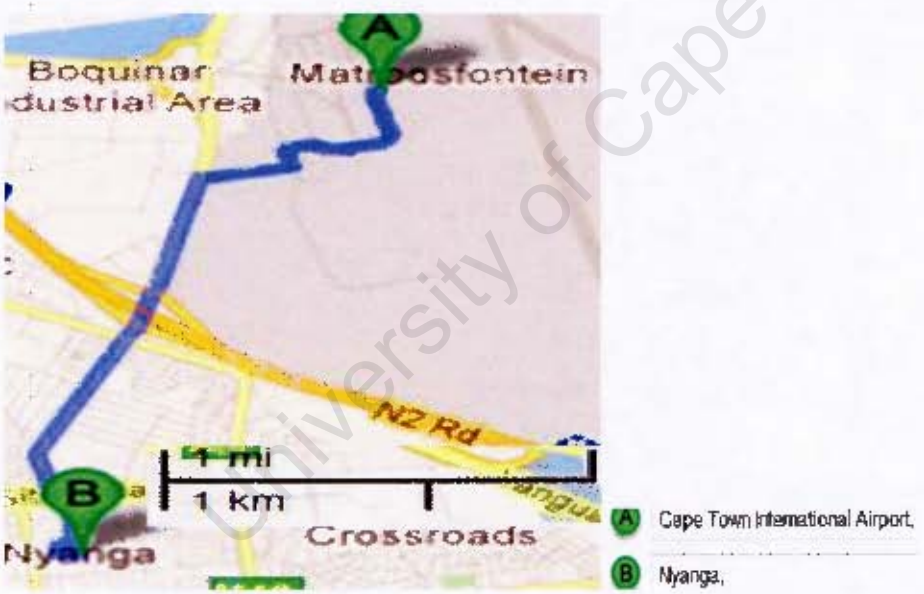

Figure 3-1: Geographical location of Nyanga from the Cape Town International Airport

In the first round sampling campaign wood samples were collected randomly from along the roadside from different caterers. This area is busy with people as householders are fully situated both sides of the road. In the third round sampling campaign, wood samples were collected only from chicken boilers as they seemed most likely to use treated waste wood. This was also along the roadside. Smoke samples used in the study were collected along the roadside where wood samples were taken while others were taken around the Nyanga Taxi rank. This is also a busy place with a lot of people (passengers) and other grocery traders.

Langa

Langa is situated just 15 to 20 kilometres from the centre of Cape Town and accessible where the N2 joins Bunga Avenue (Figure 3-2). The area was made up of singles quarters and hostels for migrant workers during the apartheid era, but has been transforming in the past two years. Langa hosts a squatter camp and it has also a vast taxi rank and a community centre (SA-Venues, 2011).

Langa was created in 1901 in the wake of the Bubonic Plague where over 500 Africans, identified as a 'health hazard', were resettled. It became the first black township in the Cape (SA-Venues, 2011). As in Nyanga, there is a vibrant informal catering economy, including braaiers of meat, sausages and sheep head, chicken boilers, African beer brewers and maize vendors..

Figure 3-2: Geographical location of Langa from the Cape Town International Airport

Langa was only visited for the third round sampling campaign. Wood and smoke samples were collected from the caterers working along roadsides, boiling maize and African beer, while some others were braaing meat. This area was busy with householders since the road passed in between two sides of occupied land by householders.

Khayelitsha

Khayelitsha is situated at 32 kilometres from the centre of Cape Town, adjacent to the N2 National Road. More than half of Cape Town's unemployed live in the area of Khayelitsha. It was created during apartheid as a dormitory area for migratory workers, today it is the biggest and youngest

black township on the Cape Flats. Its location from Cape Town International Airport can be seen in Figure 3-3.

Figure 3-3: Geographical location of Khayelitsha from the Cape Town International Airport

Five years ago, 500 000 people, constituting 51% of Khayelitsha's economically active population were unemployed, and 90% of households earned less than R 3500 per month (Benson, 2007). Many of the township's residents live in formal houses. The houses are a combination of the 1980s 'matchbox houses' and the more recent low-cost homes, and the business district is fast being developed with an open-air high street mall opening for business recently.

Khayelitsha is known to have a compromised air quality, where PM_{10} is the predominant air pollutant. One of the recorded causes is the use of wood as a fuel (Tessema, 2011; City of Cape Town, 2007)

It is known that wood is used by households for heating purposes especially in winter time (Benson, 2007; City of Cape Town, 2007). Informal caterers also make use of wood when braaing meat and sausages, boiling chicken, sheep head and maize.

In Khayelitsha, samples collected in the first round sampling campaign were taken randomly along the roadside as in Nyanga. The wood and smoke samples collected in the third round sampling campaign were collected from the Makhaza site in Khayelitsha, close to sheep head boilers and braaiers working along the roadside.

3.2.2 The peri-urban context

The townships in peri-urban areas of Cape Town have the following common features: they are surrounded by large farms and situated in the vicinity of smaller towns. In this study, Kayamandi (near Stellenbosch), Zwelethema (near Worcester) and Mbekweni (near Paarl) were chosen to represent the peri-urban areas.

Kayamandi

It is located outside of Stellenbosch about 39 kilometers from Cape Town International airport (Figure 3-4), and it was founded in 1950. Currently Kayamandi has a population of about 33000 people on 75.06 hectares. More than 65% of the population in Kayamandi experience poor living conditions in squatter camps without a proper infrastructure. Seven in ten men living in Kayamandi have TB and there is also high incidence of other chronic illness such as diabetes, epilepsy etc. There are approximately 7 000 people with full-blown AIDS in Kayamandi (ABL Development Services, unpublished). As in other townships investigated, in Kayamandi, caterers also use wood to prepare food for their clients.

Figure 3-4: Geographical location of Kayamandi from the Cape Town International Airport

In Kayamandi, wood and smoke samples were taken purposefully from the chicken and maize boilers, and sheep heads vendors. Based on visual inspection of the wood in their stocks ready to be used, they seemed to use CCA-treated wood. The samples were taken from a busy place close to Kayamandi High School and close to homes and other caterers.

Zwelethemba (near Worcester)

Worcester is a town located at about 111 kilometers north of Cape Town along the N1 (Figure 3-5). Worcester has a lot of informal settlements and townships, and there also informal caterers burning wood daily when preparing food for the people. One visited township was Zwelethemba. It is located 6 km from the centre of Worcester. The largest problem in the community is mainly related to health education for children and those living with TB and HIV/AIDS (Suzhou, 2011/November). As in other townships, caterers use wood to prepare food for their clients, whilst households use wood for heating and cooking purposes.

Figure 3-5: Geographical location of Worcester from the Cape Town International Airport

The wood samples were taken from one caterers fuel wood trolley, after considering the visual aspect of the colour of the wood. The place was busy with caterers and their clients and households around.

Mbekweni

Mbekweni is a township situated about 80 km north of Cape Town near the town of Paarl (Figure 3-6). As with other townships in urban areas, its history can be traced back to the apartheid period. It had a growing population of 24,000 people following the pattern of urbanisation and rural communities moving to populated centres for both employment and services, against a backdrop of decreasing life expectancy (Hope through action, 2010). The health of the residents is of concern: TB increased in the area by 17% from 2001 to 2002, (Hope through action, 2010). Caterers also use wood to prepare food for their clients as in other townships.

Figure 3-6: Geographical location of Mbekweni from the Cape Town International Airport

The wood samples were taken from both caterers and houses alongside the road considering the visual aspect of the colour of the wood. The place is always busy with the caterers and their clients as well as the people living around.

3.3 Sample preparation and analysis

3.3.1 Wood sampling

Sampling of fuel wood occurred in 3 urban areas including Langa, Nyanga and Khayelitsha and 3 peri-urban areas including Zwelethemba (Worcester), Mbekweni (Paarl) and Kayamandi (Stellenbosch) in the Western Cape. This occurred in three different campaigns.

In the first campaign Dr S Naidoo of the research team visited Nyanga, Khayelitsha and 5 other areas in the urban area in October 2010. He randomly collected a total of 226 wood samples: 55 from Nyanga, 31 from Khayelitsha, 45 from Malawi Camp, 45 from Blue Downs, 10 from near a Factory close to Malawi Camp, 25 from close to Airport Kaya and 15 from Jan Smut Drive. Of those areas, Nyanga and Khayelitsha were considered as representative of urban areas which means that only 86 wood samples from the first campaign were analysed, viz. 55 wood samples from Nyanga and 31 samples from Khayelitsha which were to be used as a fuel source by informal food caterers. The samples were stored in storage boxes (Figure 3-7) before transporting them to the Chemical Engineering Laboratory at the University of Cape Town.

Figure 3-7: wood samples in their storage boxes

In February 2011 one sample was collected in Kayamandi. This specimen had a dark green tint and was noticeably different in appearance from all samples previously collected in urban areas. This made us think of a second sampling campaign in peri-urban areas.

The second campaign started in March 2011 and was jointly executed by the author and Dr S Naidoo. In contrast to the first sampling campaign, wood was selected based on the visual suspect of CCA-treatment. A total of eleven samples were purposefully collected from Zwelethemba (near Worcester) (eight samples) and Mbekweni (near Paarl) (three samples). They were both from houses and from caterers' trolleys. All were planks and some of them showed the green colour. They were stored separately. The earlier Stellenbosch sample was combined with these 11 samples, all representing specimens of suspected CCA-treated wood found in peri-urban areas.

As the first campaign had been a random one in urban areas and the second one a purposive one in peri-urban areas, we thought of a third campaign in both urban and peri-urban areas which again purposefully looked for and collected fuel wood specimens that appeared to have been treated by CCA. In June 2011, 18 samples were collected from the areas sampled before, excluding Worcester and Mbekweni. In this campaign, Langa was also included as an urban area, as a collaborative study with colleagues from the Occupational Health unit had selected a site in this area. 116 wood samples (Table 3-1) from all the areas were analysed.

In each case, all samples were labelled depending on where they were collected from.

Table 3-1: A summary of number of analysed samples from each area

	urban areas			peri-urban areas			
area	Nyanga	Khayelitsha	Langa	Stellenbosch	Mbekweni	Worcestor	total
1st campaign (November/2010)	55	31	0	0	0	0	86
2nd campaign (March/2011)	0	0	0	1	3	8	12
3rd campaign (June/2011)	6	3	5	4	0	0	18
total	61	34	5	5	3	8	116

3.3.2 Smoke sampling

3.3.2.1 MiniVol air sampler

The MiniVol™ Tactical Air Sampler (TAS) (Figure 3-8) is a portable ambient air sampler for particulate matter that can also be configured for sampling various air toxics. The manufacturer claims that the patented low flow technology used in the MiniVol™ TAS was developed jointly with the U. S. Environmental Protection Agency (EPA) in an effort to address the need for portable air pollution sampling technology. The manufacturer further makes the following claims, which justified the use of this instrument for the intended purpose of collecting smoke samples near informally operating caterers:

"While not a reference method sampler, the mass concentrations of the MiniVol™ TAS give results that closely agree with reference method concentrations. Both accurate and precise, the battery operated, lightweight MiniVol™ TAS is ideal for sampling at remote sites or areas without power. The MiniVol™ TAS features a 7-day programmable timer, a constant flow control system, an elapsed time totalizer, rechargeable battery packs, and an all-weather enclosure." (Air metrics, 2002).

Figure 3-8: MiniVol Air Sampler

During the smoke sampling, the MiniVol operated without problems.

3.3.3 Equipment calibration and controlled smoke sampling

As discussed above, the MiniVol is a portable sampler to determine PM_{10} in air, for environmental quality control purposes, which loads the captured particulate matter onto a filter, allowing for further analysis.

Before using the MiniVol sampler, which was newly acquired for this study, it was compared to one of the fixed air samplers installed at different air quality monitoring sites in the city of Cape Town. During September/2010, the MiniVol was set-up close to a TEOM sampler at the Bellville South Air Quality monitoring Station. The TEOM (Tapered Element Oscillating microbalance) is a fixed air sampler that provides a continuous direct mass measurement of PM_{10}, $PM_{2.5}$, and PM_1 particulate loaded on filters. Sampling was performed over a 24 hour period. In both cases the particulate matter was collected on filter papers. Gravimetric analyses of the loaded filters give the particulate matter concentrations in the volume of air that passed through the filter papers. This is known as PM_{10} concentrations and reported in $\mu g/m^3$.

The PM_{10} concentration read from the TEOM was 61.19 $\mu g/m^3$ while the MiniVol showed 58.37 $\mu g/m^3$. The difference between the TEOM and MiniVol 24-h average concentration measurements was 2.82 $\mu g/m^3$ with the TEOM yielding slightly higher results; a similar result to the Baldauf et al. (2001) study, which an average difference of 3 $\mu g/m^3$ (with the TEOM sampler also reporting higher values). According to Baldauf et al (2001), the collection efficiency of the MiniVol is influenced by wind speed. The average differences between the two samplers were found to be reasonably small, supporting the plan to use the MiniVol to collect particulate matter in smoke from wood fires. The particulate matter was collected on quartz filter media. The loaded filters were weighed to determine its PM_{10} concentration and then analysed in the laboratory for Cr, Cu and As, after digestion.

In the next preparatory experiment, the MiniVol was placed close to a wood fire to sample its smoke. Particles in the smoke were thus collected on filter papers and analysed. The wood considered to be untreated (sample 55 and 51) both from Nyanga, were burnt after the CCA-treated wood burning and they showed inconsistent results (Table 3-2). The wood that was also burnt for collection was from an H5 specimen collected during the second sampling campaign from Stellenbosch and an H2 collected from the Epping Timber Treatment. This was done to confirm that elevated CCA concentrations would show in smoke collected on the filters when CCA-treated wood was burnt.

Table 3-2: CCA levels in the smoke from typical wood burning

Sample burned	Time (h)	mass of PM_{10} (mg)	PM_{10} ($\mu g/m^3$)	Cr ($\mu g/m^3$)	Cu ($\mu g/m^3$)	As ($\mu g/m^3$)	Cr: Cu : As ratio
H5 (Stellenbosch)	0.58	0.25	1387.9	6.52	1.53	51.91	4: 1: 34
(H2)	0.57	0.14	795.4	7.39	1.42	19.17	5: 1: 14
Sample 55	0.20	0.01	161	24	83.5	6	0.3: 1: 0.1
Sample 51	0.10	0.01	321	32	9	16	3.5: 1: 1.7

It was noted that the concentration of arsenic volatilised from typical CCA-treated wood ranged between 19 and 52 $\mu g/m^3$. This concentration depended on the distance between the fire and the MiniVol sampler and the intensity of the fire. These results obtained tied in with the results reported in literature reviews on the MiniVol performance by Baldauf et al (2001), and therefore showed that the MiniVol Sampler was suitable to collect smoke samples for this study.

3.3.3.1 Ancillary equipment

The filters used in the study were made of quartz. They were chosen for their resistance to carbon damage; complete digestion of the filter by acid was not required for Cr, Cu and As determination in captured particulate matter. The filters were 47 mm in diameter and the pore size was 0.5 µm, which is acceptable for PM_{10} sampling. The filters were pre-weighed using a 5 decimal microbalance and kept in clean petri dishes. During sampling, the filter was placed in the filter cassette and put into the inlet containing PM_{10} impactor. After checking that everything is in order for the MiniVol, the start button was pressed. After the sampling, the loaded filters were removed from the cassette and put in the petri dishes to transport them to the laboratory for re- weighing (Figure 3-9). After this, the filter containing the sample was ready for analysis.

a) Decimal microbalance

b) Loaded filters in petri dishes

Figure 3-9: Ancillary equipment

3.3.3.2 Smoke sampling locations

The campaign of smoke sampling started in May 2011 and was done in the same areas where the wood samples had been taken. The areas where wood samples were taken from were revisited for smoke sampling, excluding Zwelethemba in Worcester and Mbekweni in Paarl. Samples from Langa were included under programme of joint wood and air sampling listed below. A total of 19 smoke samples were collected, but one of them was damaged during transportation which allows the researcher to consider 18 samples composed as follows:

- 8 from Nyanga (5 not far from the wood fires and 3 around the Taxi rank)

- 3 samples from Khayelitsha (close wood fires)

- 4 samples from Langa (close wood fires) and

- 3 samples from Kayamandi (Stellenbosch) (close wood fires)

The smoke samples were collected over duration of between 1-4 hours. The height at which samples were taken from was approximately 1.50 m and the distance from the fire was generally 2 m except for three samples taken from Nyanga around the Taxi Rank where it was farther (±100 m) from the fire. The detailed information about the conditions in which the smoke samples were taken from is fully described in Appendix 1.

This section describes the procedures used to calculate the quantity of the CCA metals in the smoke.

After performing preliminary experiments on wood and filters, it was confirmed that the same microwave digestion method is applicable to both wood and smoke samples.

After the filters were weighed upon return from the field, they were kept in clean petri dishes until the microwave digestion.

Very small quantities of smoke were collected. The average weight of an empty filter is 147.14 mg while the sampled filters on average weighed 147.69 mg. The average of the weight of PM collected was approximately 0.55 mg.

The sampled filter was digested by nitric acid as stated above. After the digestion, the digest was run through ICP-AES analysis for total metal analysis.

The reading from ICP was in ppb (part per billion). Where the ICP reported negative values, the samples were considered not to contain any metals. The ICP readings needed to be converted to a concentration of metal in particulate matter, expressed in $\mu g/m^3$ of air. To determine this, the following 4-step calculation procedure was used.

3.3.4 Joint wood and air sampling

Part of the smoke sampling was conducted jointly with the third wood sampling campaign, with the aim of observing whether there was a correlation of both metal contents in wood and smoke samples. Corresponding wood and smoke sample numbers are presented in Table 3-3.

Table 3-3: Wood and smoke samples taken at the same time

Place	Date	Wood sample number	smoke sample number
Langa	27.06.2011	1, 2	9
	29.06.2011	-	10
	30.06.2011	-	11
	2.07.2011	3, 4, 5	12
Stellenbosch	2.08.2011	16, 17, 18	13
	3.08.2011	15	14
	27.08.2011	-	15
Khayelitsha	20.8.2011	6	-
		-	16
		7, 8	17, 18

The numbering of all the analysed samples is available in Appendix 1

3.3.5 Wood samples

To analyse wood samples for total concentrations of Cr, Cu and As, finely ground sawdust produced from the samples were digested in nitric acid according to EPA Method 3051, followed by ICP analysis. The following sub-sections describe the extraction of material from the collected specimens, the further sample preparation, as well as the ICP analysis method.

3.3.5.1 Wood size reduction

In order to analyse the wood samples, a drill press flitted with a 15 mm circular hollow bit was used to extract wood chips from the wood. The objective was to obtain a representative chip sample at depth > 40mm as this is the optimum penetration depth for CCA-treatment (Figure 3-10)

Figure 3-10: chip wood samples

The chips were further reduced into sawdust (size <0.25 mm), as recommended by Stilwell et al. (2003) using a grinder (type: Retch ZM-1: the Ferguson Industrial Equipment Group, Johannesburg 2000). All the sawdust samples were kept in plastic bags and labelled according to where the sample was collected from (Figure 3-11).

Figure 3-11: The sawdust wood samples in clean plastic bags

3.3.5.2 Microwave wood digestion

A closed vessel microwave digestion system (MARS Xpress CEM-USA) was used to digest the wood samples. It consists of a compact terminal touch screen display with operator selectable 0- 1600 W output, temperature control up to 240°C, pressure control up to 800 psi, layer-PTFE coated microwave cavity, HPR/ 1000/10S Rotator and 100ml Teflon vessels (Figure 3-12)

Figure 3-12: A closed microwave digestion system

Due to the large number of samples and to the prior use, the vessels were soaked in a mixture of nitric acid and hydrochloric acid overnight to prevent contamination and finally, the vessels were rinsed with ultrapure water three times.

0.25 g of sample was put into each Teflon vessel alongside with 10 ml of analytical grade 55% HNO_3. Then the vessels were capped, placed into the microwave system, and digested. The samples were digested using the protocol summarized in Table 3-4. After cooling to room temperature the sample digests were carefully transferred to 25 ml flasks and diluted to the final volume using ultrapure water. This was performed in a fume cupboard. The samples were then refrigerated at 4 °C until analysis.

Table 3-4: Microwave wood digestion description

Step	Time(min)	Power(W)	Temperature (°C)	Pressure (psi)
1	15	1600	192	200
2	30	1600	204	394

3.3.5.3 Determination of total metal concentration using ICP-AES (EPA SW 846 Method 6010B)

ICP-AES analysis quantitatively determines trace elements, including metals, in solution. It operates on the principle of atomic emission by atoms ionized in the argon plasma. Light of specific wavelengths is emitted as electrons return to the ground state of the ionized elements,

quantitatively identifying the species present. This method is applicable to the three CCA metals of concern in this project. ICP-AES requires digestion (or an equivalent processing) of samples prior to analysis. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions (Wu et al., 2006). Table 3-5 lists the recommended analytical wavelengths and estimated instrumental detection limits for CCA metals in clean aqueous matrices.

Wu et al. (2006) reported that the detection limits in the ICP-AES method are sample dependent and may vary as the sample matrix varies.

Table 3-5: Recommended Wavelength and Estimated Instrument Detection Limit for CCA metals

(Wu et al., 2006)

Element	Recommended Wavelength (nm)	Estimated Instrument Detection Limit (µg/l)
Arsenic	193.696	3.5
Chromium	267.716	4.7
Copper	324.754	3.6

The samples in this study were analysed by ICP-AES Varian 730-ES. Concentrations were reported in ppm (part per million) and had to be converted to mg of metal/kg of wood.

The concentration of metal in the wood samples was determined as follows:

Metal [ ] in wood (mg/kg)=ppm reading (mg of metal /L of solution) × *volume of dilution (25 mL of solution x 1 L / 1000 mL) / Sample mass (g of wood x 1 kg / 1000 g))*

3.3.5.4 Determination of total metal concentration in PM10

Metal concentration (mg/kg) =

$$\frac{\textit{ppb (µg of metal/L of solution)} \times \textit{volume of dilution (mL of solution)}}{\textit{Sample mass (g of } PM_{10}\textit{)} \times 1000}$$

Relation (1)

The answer is found in mg of metal per kg of PM_{10}

The following step is to determine the level of metal contained in a particular collected PM_{10} concentration when a particular wood is burned. This is obtained by firstly find the concentration of PM_{10} by the following formula:

3.3.5.5 Calculation of volume of air sampled

From the Air metrics procedures, calculations are done as follows:

$Q_{act}= (m_{vol}\times Q_{ind} + b_{vol}) \sqrt{P_{std}/P_{act}\times T_{act}/T_{std}}$ (1)

$I_{sp}=[5.0\times(\sqrt{P_{act}/P_{std}\times T_{std}/T_{act}})-b_{vol}]/m_{vol}$ (2)

Where:

Q_{act}: Actual Flow Rate, liters/min

Q_{ind}: Rotameter Indicated Flow Rate, liters/min

m_{vol} = slope of the least square line and equals to ***1.1409*** for the Minivol used in this study

b_{vol} = intercept of the least square line and equals to ***-0.4251*** for the Minivol used in this study

I_{sp} = Calculated Rotameter Setpoint, liters/min

P_{std} = Standard Atmospheric Pressure, (760 mm Hg)

T_{std}= Standard Temperature, (298 °K)

P_{act}=Actual Ambient Pressure, (mm Hg)

T_{act}=Actual Ambient Temperature, (°K)

To calculate the volume of air that passed through the filter during the sampling period at actual ambient conditions, **Vact** (in cubic meters), was done as follows:

$Vact= (60\ min/hr\times Qact\times thr)/1000l/m^3$

Where thr = sampling period, in hours

The units of Vact are *cubic meters*.

3.3.5.6 PM Concentration Calculation

To calculate the concentration of PM, divide the net mass gain of the filter by the volume of air that passed through the filter.

$PM_{act} = M_{PM}/V_{act}$ *Relation (2)*

Where PM_{act} = PM concentration, in micrograms (µg) per cubic meter (actual)

M_{PM} = Mass of particulate matter collected on the filter, in micrograms (µg)

3.3.5.7 Metal Concentration Calculation

After finding the concentration of PM_{10}, the quantity of metal present in that typical PM_{10} concentration was calculated as follows:

Metal [ ] in $\mu g/m^3$ = [Relation (1) × relation (2)]/1000000 or,

Metal [ ] in air ($\mu g/m^3$) = [PM_{act} (mg) × Metal [ ] in wood (mg/kg)]/1000000

The experimental work was structured such the research questions in Section 3.1 were interrogated. The schematic diagram (figure 3-12) outlines how each of the key questions coincides with an aspect of the experimental work done.

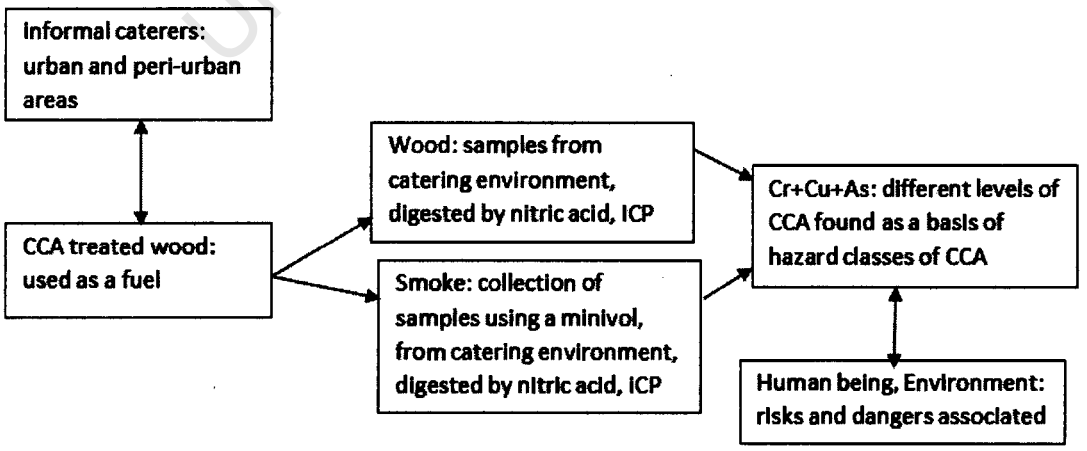

Figure 3-13: Outline of the research methodology

3.4 Ethical conformance

To ensure that proposed research conforms to acceptable ethical standards, the Engineering and Built Environment (EBE) faculty stipulates that research that proposes the involvement of human participants for data collection undergo an ethics review. The research undertaken herein however did not require human participation for data collection and as such approval from the EBE Ethics in Research Committee (EiRC) was not necessary. However, the prescribe ethics form was filled completed and is included in Appendix 3.

4 Results

This chapter presents the analysis results for both the wood and smoke samples taken. Results from different wood digestion methods were compared to each other to determine the best digestion method to be used for this study. Once the best wood digestion method was established, the collected wood samples were analysed for their Cr, Cu and As content and the results are tabulated in this chapter. Finally, PM_{10} and metal concentrations in the smoke samples taken are presented, both for an experiment under controlled conditions, and for field sampling.

4.1 Analysis of CCA-treated wood

The aim of this study was to ascertain whether the wood used as fuel by informal caterers posed unseen risks through exposure to arsenic. This is because fuel wood of different hazard classes of CCA-treatment might be available to such caterers where it might be used in combination with harvested wood. Assuming that the average density of the wood is 900 mg/m^3, the estimated levels of different hazard classes of CCA-treated wood are calculated (Table 4-1) based on their typical dosage (Table 2-2), and the impregnation concentrations reported by Romeo the manager of the Timber Preservation Services (TPS) in Epping on the 5th of February 2011, to be 140.2, 91.8 and 135.3 g/kg of Cr, Cu and Arsenic respectively.

Table 4-1: Estimated compositions of Tanalith-impregnated timber

Wood category	Cr (mg/kg)	Cu (mg/kg)	As (mg/kg)
H2	935	612	902
H3	1246	816	1203
H4	1869	1224	1804
H5	2492	1632	2405
H6	3739	2448	3608

The following paragraphs detail the metal analysis results for all samples extracted from collected fuel wood specimens. The results are arranged chronologically in order of sample collection.

Levels of CCA in the samples collected in the first sampling campaign in Nyanga and Khayelitsha were all well below reliable detection limits of 5 ppm in the digestate, equivalent to 500 mg/kg of wood. The elements of concern seemed to be present in most of these samples, indicatively at mean

values of 11.8 ± 11.6, 11.0 ± 4.6 and 6.2 ± 3.0 mg/kg of Cr, Cu and As, respectively. These levels are 10-100 times lower than those typical of the lowest dosage of CCA-treated wood (H2) (Table 4-1).

Upon advice from the treatment plants, it was decided to attempt a second sampling campaign, armed now with knowledge that treated wood was of a specific functional design and showed a green tint once treated. As shown by the metal concentrations shown below, CCA-treated wood was found during the second and third round of sampling. This supported the need to use visual inspection during sampling.

A total of 12 timber specimens were collected during the second sampling campaign. As shown in Figure 4-1, eight specimens were CCA-positive and were collected from the following areas: one sample from Stellenbosch, five from Worcester and two from Mbekweni. The mean Cr, Cu and As levels in the eight samples identified as treated were 1946 ± 2123, 849 ± 592 and 1427 ± 1167 mg/kg, respectively.

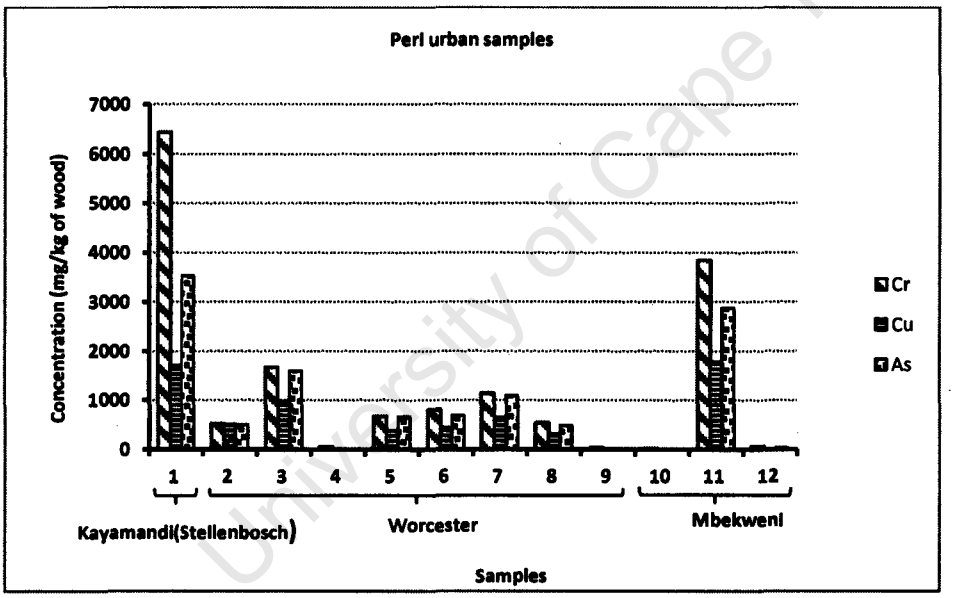

Figure 4-1: Cr, Cu and As concentrations in collected samples from the 2nd sampling campaign

Of the 18 samples collected during the 3rd sampling campaign, eight contained Cr, Cu and As at levels typical of treated wood (Figure 4-2). Two of these 6 samples were from Nyanga, two from Khayelitsha, one sample from Langa, and three samples from Stellenbosch. The mean Cr, Cu and As levels of these eight samples were very similar to those of the eight positively identified samples of campaign 2, at 2035 ± 917, 871 ± 344 and 1645 ± 710 mg/kg, respectively.

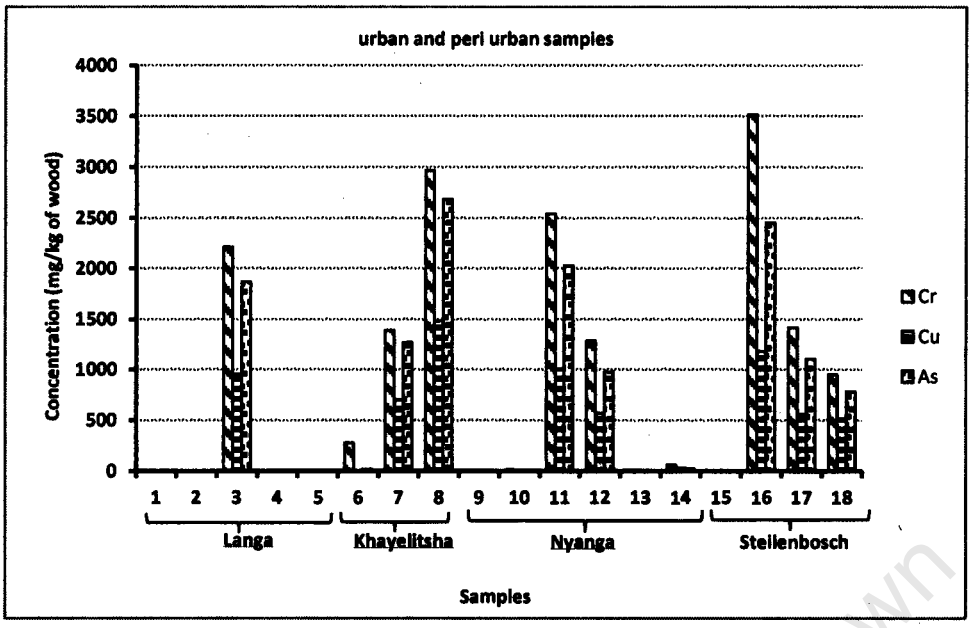

Figure 4-2: Cr, Cu and As concentrations in collected samples from the 3rd sampling campaign

Table 4-2 presents a summary of the results for all three sampling campaigns. A statistical interpretation should not be undertaken as the initial sampling campaign was randomly performed without the knowledge of green tinted timber as a visual indicator of CCA presence, whilst in the 2nd and 3rd campaigns only samples that appeared suspect were taken.

Table 4-2: Summary of wood sampling and number of CCA treated samples in the study

	urban areas			peri-urban areas				
area	Nyanga	Khayelitsha	Langa	Stellenbosch	Mbekweni	Worcester	total	CCA treated
1st campaign (November/2010)	55	31	0	0	0	0	86	(0)
2nd campaign (March/2011)	0	0	0	1(1)	3(2)	8(5)	12	(8)
3rd campaign (June/2011)	6(2)	3(2)	5(1)	4(3)	0	0	18	(8)
total	61(2)	34(2)	5(1)	5(4)	3(2)	8(5)	116	(16)

(): number of samples classified as 'CCA-treated' by site

Table 4-3 gives an indication of categories of CCA-treated wood into which the 16 samples found to be treated fall, based on the Cr, Cu and As concentrations measured. Six were within the H2 category (37.5%), three within H3 (18.7%), three within H4 (18.7%) and four displayed levels typical of H5 treatment (25%). 3/4 samples in the H5 category (75%) and 1/3 in the H4 category (30%) were from peri-urban areas.

Table 4-3: Summary of Cr, Cu and As levels, likely treatment categories and recipes of treated wood samples collected in the study areas

	area	Cr(mg/kg)	Cu(mg/kg)	As(mg/kg)	CCA category	Cr: Cu: As ratio	recipes
	stellenbosch	6438	1711	3531	H5	3.7: 1 : 2	unkown
	stellenbosch	3517	1179	2450	H5	3.0: 1: 2	unkown
peri-urban	stellenbosch	1416	559.9	1103	H3	2.5: 1: 2	unkown
	stellenbosch	949.7	518.7	783.8	H2	1.8: 1: 1.5	CCA-C
	worcester	511.0	512.4	501.1	H2	1.0:1.0:1	unkown
	worcester	1666	984.3	1593	H4	1.7: 1: 1.6	CCA-C
	worcester	662.9	387.6	666.9	H2	1.6: 1: 1.7	CCA-C
	worcester	786.6	447.5	686.5	H2	1.8: 1: 1.5	CCA-C
	worcester	1127	645.2	1087	H3	1.7: 1: 1.7	CCA-C
	worcester	535.4	317.8	481.2	H2	1.7: 1: 1.5	CCA-C
	Mbekweni	3844	1788	2871	H5	2.1: 1: 1.6	CCA-C
urban	Langa(zone 14)	2211	951.8	1868	H4	2.3: 1: 1.9	unkown
	Khayelitsha	1390	703.2	1270	H3	1.9: 1: 1.8	CCA-C
	Khayelitsha	2963	1479	2679	H5	2.0: 1: 1.8	CCA-C
	Nyanga	2543	1007	2028	H4	2.5: 1: 2.0	unkown
	Nyanga	1288	570.3	977.9	H2	2.2: 1: 1.7	unkown

Based on the Cr:Cu:As ratios determined, it appears that the majority of the sixteen samples identified as treated had been subjected to a *Tanalith* or CCA-C treatment.

4.1.1 PM_{10} and metal concentrations for smoke sampling

Of the 19 smoke samples collected, only 18 were analysed while one was damaged during transportation.

Samples were taken according to predetermined conditions in terms of time the sampler was run, the distance the MiniVol was from the fire and during certain climatic conditions (temperature and pressure) (appendix 1).

PM_{10} results around the taxi rank were found to be considerably lower comparing to the PM_{10} close to wood fires (Figure 4-3). (The average of the PM_{10} over the sampled areas was 1685 $\mu g/m^3$) The lowest concentration was found around Nyanga taxi rank and it was 33 $\mu g/m^3$, while the highest is 8139 $\mu g/m^3$ found in Khayelitsha close to wood burning fires.

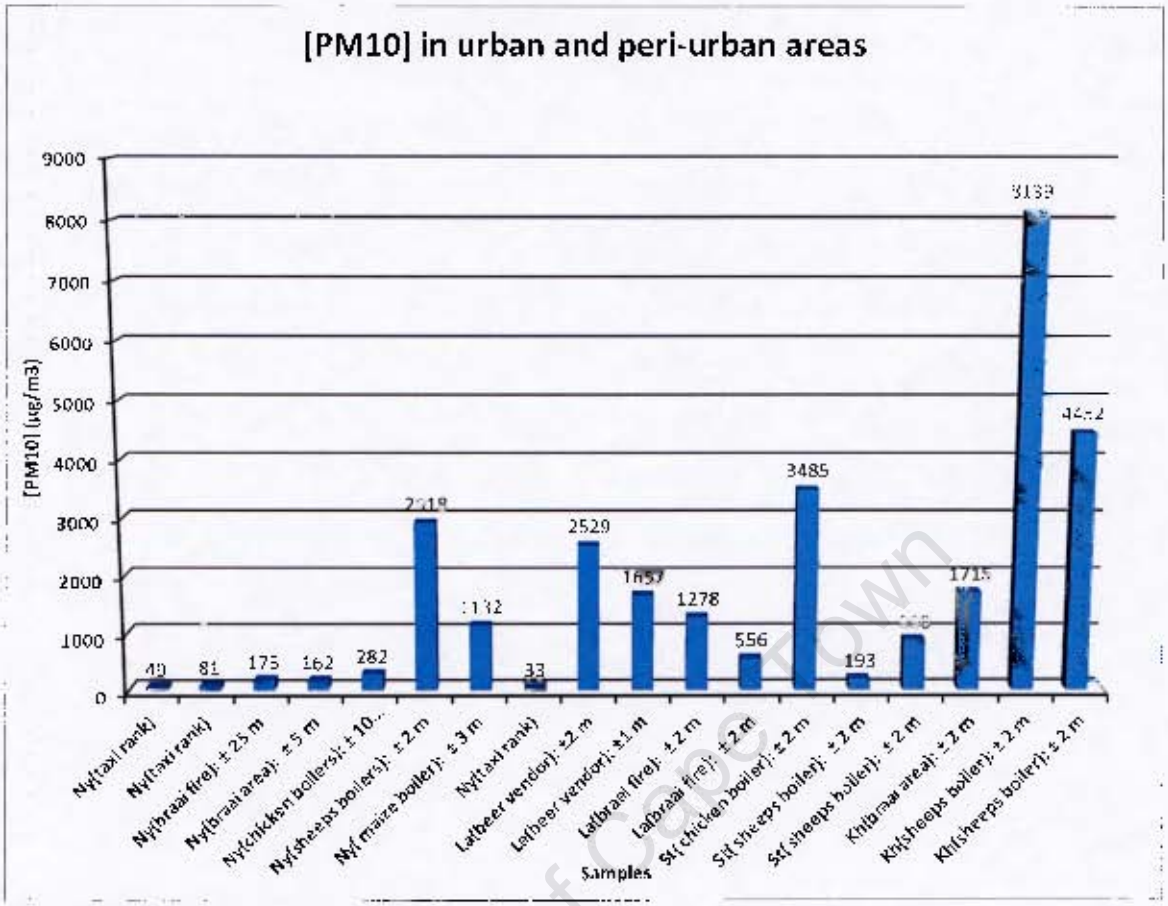

Figure 4-3: PM_{10} concentration in urban and peri-urban areas

After the measurements of PM_{10} further analysis was done to calculate the arsenic concentration in each. Arsenic was detected in 15 samples with the lowest being 0.1 and the highest 11.8 µg/m^3 of arsenic (Figure 4-4). The average of the arsenic positive samples was 2 µg/m^3 of arsenic, 1.7 µg/m^3 of chromium and 0.5 µg/m^3 of copper.

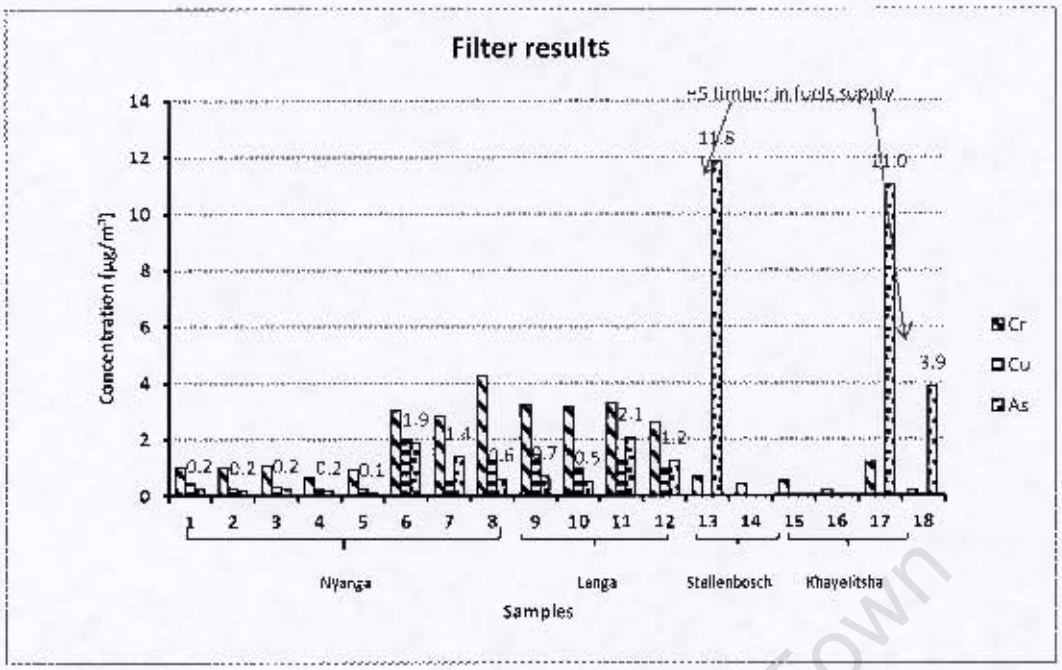

Figure 4-4: CCA concentrations in smoke samples from in urban and peri-urban areas

The highest arsenic concentration was measured near wood burning fires in Stellenbosch (11.8 µg/m^3) while chicken was boiled in closed pots; the lowest arsenic level (0.1 µg/m^3) was measured from wood burning in Nyanga. Two samples from Stellenbosch and one from Khayelitsha did not show any arsenic, those are samples 14, 15 and 16. Considering other CCA constituents (chromium and copper), it was noted that those elements are also present in the smoke (Table 4-4).

Table 4-4: Cr: Cu: As ratios for the smoke samples

Area	Sample number	Cr (µg/m³)	Cu (µg/m³)	As (µg/m³)	Cr: Cu: As ratio
Nyanga(taxi rank)	1	1.0	0.4	0.2	2.3: 1: 0.5
Nyanga(taxi rank)	2	1.0	0.3	0.2	3.7: 1: 0.6
Nyanga(braai fire)	3	1.1	0.3	0.2	3.7: 1: 0.8
Nyanga(braai area(100m))	4	0.7	0.2	0.2	3.4: 1: 0.8
Nyanga(braai fires and chicken boilers)	5	0.9	0.2	0.1	3.8: 1: 0.4
Nyanga(sheeps boilers(2 m))	6	3.0	2.0	1.9	1.5: 1: 0.9
Nyanga(maize boiler(3m))	7	2.8	0.5	1.4	5.4: 1: 2.7
Nyanga(taxi rank)	8	4.3	1.3	0.6	3.4: 1: 0.5
Langa(beer vendor)	9	3.3	1.5	0.7	2.2: 1: 0.5
Langa(beer vendor)	10	3.2	0.9	0.5	3.3: 1: 0.6
Langa(braai fire)	11	3.3	1.3	2.1	2.6: 1: 1.6
Langa(braai fire)	12	2.6	0.9	1.2	2.8: 1: 1.3
Stellenbosch(chicken boiler)	13	0.7	0.0	11.8	_
Stellenbosch(sheeps boiler)	14	0.4	0.0	0.0	_
Stellenbosch(sheeps boiler)	15	0.5	0.0	0.0	_
Khayelitsha(braai area)	16	0.2	0.0	0.0	_
Khayelitsha(sheeps boiler)	17	1.2	0.0	11.0	_
Khayelitsha(sheeps boiler)	18	0.2	0.0	3.9	_

4.2 Concluding note on presented results

In summary, this chapter has presented evidence that CCA-treated timber could be found in fuel supplies of both urban and peri-urban informal caterers, and of households in the latter case. Additionally, several smoke samples taken near such fires showed elevated Cr, Cu and As levels, with the As:Cu ratio increasingly significantly in a number of these samples. An interpretation of the results presented in this chapter will follow in chapter 5, considering also evidence from joint wood and smoke sampling, where this could be undertaken.

5 Discussion

5.1 Introduction

This chapter starts by reviewing the sampling campaigns followed, the various wood digestion methods tested, and the verification of the instrumental analysis methods used for this study. Once trust in the methods and procedures is established, the chapter proceeds to discuss the significance of findings converning Cr, Cu and As concentrations documented first the wood and next in the smoke samples.

5.2 Method validation and verification

Two different sampling approaches were used in this study: in the first campaign a large number of fuel wood samples were randomly collected, whilst in the 2nd and 3rd campaigns fuel wood specimens with a green tinge were collected. During the first campaign, sampling was done without knowing that treated wood had characteristic appearances and that it could be identified by a treatment plant catalogue. None of the 86 samples tested in the first campaign showed Cr, Cu or As levels typical of treated wood. Later visual inspection of fuel supplies of caterers in urban areas confirmed that 'green tinged' pieces of wood are seen infrequently-possibly occurring in the range of 1/100 to 1/1000 in fuel stockpiles.

Sampling theory warns that significant variance can be introduced during sample processing. The focus of this investigation was not a precise determination of metal concentrations in fuel wood, but rather the detection of prior CCA-treatment followed by a broad categorization (in terms of treatment levels H2-H6). As such, the sample preparation did not have to pay detailed attention to the resulting variance. The generation of shavings with a drill would have introduced some variance by drilling to different depths: it is likely that CCA concentrations are higher closer to the surface. Furthermore, milling to a fine powder should however have homogenized the samples and thus resulting in the 0.25 g sample ultimately digested to be sufficiently representative of its respective timber sample.

The analysis method used in this study *(US EPA Method 3051)* was performed according to the instructions and no solid residues remained. There was some experimentation with the calibration of the ICP-AES *(EPA SW 846 Method 6010B)* esp. in campaign 1, as the expected CCA concentrations

were not yet known. Generally though, for digestate metal concentrations > 5 ppm the error in repeat analyses was acceptable at less than 5%. For digestions of 0.25 g of sample diluted into 25 ml, this translates to a cut-off concentration of metal in wood of 500 mg/kg – well below the H2 range (as reported in Table 4-1) but well above natural background levels varying from less than 1 to 120 mg/kg (Eisler, 1998).

The standards used in the ICP-AES sample analysis were approved by SABS.

5.3 Fuel wood in the urban context

In townships within the urban area, roadside catering activities in Nyanga, Khayelitsha and Langa were sampled. In all these areas, it was observed that barbequing ("braaing") activities make use of harvested wood, even though in most cases the fire is started with dry wood that is either painted or from old pallets. Very little harvested wood is used for other cooking such boiling. The pallet wood from adjacent light industrial areas, as well as demolition timber, are dominant in these areas as there are no forest plantations within the boundary of the city (Nissing and Von Blottnitz, 2007). The kind of waste wood used is shown in Figure 5-1.

Figure 5-1: Two wood stocks for informal caterers in Nyanga

Even though during the first campaign, samples from Nyanga and Khayelitsha did not show CCA-treated wood, during the third campaign CCA-treated wood specimens were collected there. This showed that CCA- treated wood is available and used together with other fuel wood by the informal caterers. Of three suspect samples collected from Khayelitsha, two were CCA-positive, two out of six samples collected from Nyanga were positive while one of five samples from Langa was CCA-positive (Figure 4 2).

The study found wood pallets to be the predominant source of wood fuel amongst informal caterers in Nyanga, Khayelitsha and Langa. These wood pallets are actually discarded by industries after re-use and intended for disposal mainly due to breakage as the wood is of inferior quality. They are not manufactured to last for long and break quickly. Significant quantities of discarded pallet wood can easily be sourced by entrepreneurs or those in need of wood fuel. The pallets are not CCA-treated, which might be the reason why in those areas, CCA-treated wood is not so frequent. The samples collected during the first sampling campaign were small light weight samples, easily parted with by the caterer or end-user (Figure 4-2). Of 100 tested samples collected from these urban areas, 14 were purposefully picked pieces with a particular appearance and only 5 samples tested positive for CCA.

Generally, the caterers use the cheaper waste wood to start the fire. Only those who barbeque meat use harvested wood, as waste wood reportedly produces unpleasant flavours on the meat. The reason is that the waste wood burns more easily than the harvested wood. It is important to note that even when harvested wood is burned, more than 75 different chemicals are produced (Schiefer *et al.*, 1997). Waste treated wood would however produce more dangerous chemicals when compared to harvested wood. Also the informal caterers in the urban area live far from the forests and the harvested wood is not available to them easily.

Eisler (1998) reported that trees from non-contaminated areas had usually less than 1 mg/kg (dry weight) of arsenic. However Pine (*Pinus silvestris*) could have 22 mg/kg (fresh weight) when the soil is contaminated to 120 mg/kg. It is probable that the indicative concentrations of 11.8 ± 11.6, 11.0 ± 4.6 and 6.2 ± 3.0 mg/kg of Cr, Cu and As obtained from Nyanga and Khayelitsha in the first sampling campaign reflect the natural background levels. The study done by Solo-Gabrielle et al. (2002) reported that wood with such concentrations does not result in a hazardous material as defined by the regulatory criteria in USA. However, treated wood should not be mixed with untreated wood (Khan et al., 2004; Solo-Gabrielle et al., 2002).

5.4 Fuel wood in the peri-urban context

Eleven out of sixteen tested samples collected from peri-urban areas were CCA containing. In Worcester, Mbekweni and Kayamandi, CCA-treated wood used for fuel is sourced from construction of low-cost houses (Figure 5-2), and from fencing initially used for homes and farms. These wooden fences are replaced by concrete walls or metal fences. It is reported that 'the CCA level in wood falls off due to leaching by rain water and the aging of the wood' (Moghaddam &Mulligan, 2008). Despite this, high levels of chromium, arsenic and copper were detected. CCA-treated wood was substantially more frequently encountered than in the urban areas and therefore health risks to those using the wood as fuel should be assessed; CCA-treated wood should normally not be handled without safety equipment (Martin, 1998).

The CCA levels found in many of the peri-urban area wood samples (summarized in Table 4-3) are not far from the results obtained by Stillwell et al. (2003), as summarised in section 2.3.4.

By comparing the green coloration of the waste pile from construction wood found in Worcester (Figure 5-2a), the planks found together with harvested wood ready to be used by caterers (Figure 5-2b), and waste wood found in a Stellenbosch caterer's fire (Figure 5-2c), one can easily relate them to treated wood from the treatment plant (Figure 5-3).

(a)

(b)

(c)

Figure 5-2: Photos of fuel wood in peri-urban areas

(a): waste pile from construction, (b): mixed with vegetation wood, (c): wood fires at Stellenbosch

Figure 5-3: Photo of treated wood from Epping wood treatment waiting for customers

The availability of such treated wood in the peri-urban areas could possibly be related to construction and development (building of houses) activities happening on the larger open pieces of

land characterising the peri-urban context. In addition, poles from agricultural and fencing use appear to be regarded as useful fuel wood when they are discarded after use.

5.5 Arsenic in the smoke from wood combustion

This section interprets and analyses the smoke samples from wood combustion. It starts with the levels of PM_{10} in the smoke in the working environment. The significance of the determined As concentrations is discussed next, including considerations of volatilisation of arsenic. Finally, the possible presence of arsenic levels in the bottom ash is considered, based on the literature as such ash was not analysed.

5.5.1 Levels of PM_{10} in the smoke

One of the air pollutants that is classified as both a primary and secondary pollutant is particulate matter (WHO, 2005). Particulate matter consists of liquid or solid particles which are suspended in the air. As stated above in section 2.5, these particles are categorized by size, thus particulates with an aerodynamic diameter of less than 10 microns are known as PM_{10}.

In general, the use of treated wood generates a black smoke with a characteristic strong smell. This was initially noted during preliminary experiments when burning treated wood. Because of this smell, its use is mainly confined to applications involving boiling in closed vessels such as sheep-head preparation, chicken and maize boiling and brewing as seen in Figure 5-2(c). Natural wood does not produce this distinctive smoke and is generally preferred for grilling and barbequing as it does not adversely affect the taste of the food being prepared. However during the rainy season, the use of treated wood increases as natural wood is wet and is difficult to ignite. As reported in the literature, wood burning is one source of the PM_{10} in the ambient air (City of Cape Town, 2007).

The Department of Environmental Affairs and Tourism has established the National standards in South Africa for the permissible concentration of PM_{10} in the ambient air (25 °C and 101.3 Kpa) to be 120 $\mu g/m^3$ as the daily 24 hour average (City of Cape Town, 2007). The City of Cape Town has adopted the UK 24 hour daily average of 50 $\mu g/m^3$ when determining PM_{10} guideline exceedences in the city. It was reported that PM_{10} exceeds the daily standards more often in Khayelitsha than at any

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Appendix 1: Smoke sampling and analysis

Filter no.	Area / Activity	Distance from the fire source	Time start	Time end	diff.in time	W F bef(mg)
1	Nyanga (taxi rank)	_	13:28	17:28	4	146.65
2	Nyanga (taxi rank)	_	09:15	13:15	4	147.56
3	Nyanga (braai fire)	± 25 m	13:35	16:35	3	146.55
4	Nyanga (braai area(100m))	± 5 m	12:20	16:20	4	147.61
5	Nyanga (braai fires and chicken boilers)	± 10 m	10:40	14:40	4	147.13
6	Nyanga (sheeps boilers(2 m))	± 2 m	14:12	15:12	1	147.35
7	Nyanga (maize boiler(3m))	± 3 m	12:38	13:38	1	146.65
8	Nyanga (taxi rank)	_	11:20	12:20	1	147.15
9	Langa (beer vendor)	± 2 m	11:25	12:25	1	146.33
10	Langa (beer vendor)	± 1 m	10:20	11:20	1	147.31
11	Langa (braai fire)	± 2 m	10:48	11:48	1	147.65
12	Langa (braai fire)	± 2 m	09:33	10:33	1	147.6
13	Stellenbosch (chicken boiler)	± 2 m	13:06	14:06	1	147.83
14	Stellenbosch (sheeps boiler)	± 2 m	11:42	12:42	1	147.03
15	Stellenbosch (sheeps boiler)	± 2 m	13:19	13:59	0.66	147.26
16	Khayelitsha (braai area)	± 2 m	11:30	12:30	1	147.56
17	Khayelitsha (sheeps boiler)	± 2 m	12:35	13:35	1	146.24
18	Khayelitsha (sheeps boiler)	± 2 m	13:40	14:40	1	147.22

Filter no.	W F af(mg)	Mass of PM10(mg)	Pstd(mmHg)	Pact(mmHg)	Tstd(K)	Tact(K)	m vol	b vol	Qind(lpm)	Qact(lpm)	Vact(m3)
1	146.71	0.06	760	770.64	298	288	1.1409	-0.4251	5	5.2	1.2
2	147.66	0.1	760	777.48	298	288	1.1409	-0.4251	5	5.1	1.2
3	146.71	0.16	760	779	298	290	1.1409	-0.4251	5	5.1	0.9
4	147.81	0.2	760	781.28	298	290	1.1409	-0.4251	5	5.1	1.2
5	147.48	0.35	760	775.96	298	292	1.1409	-0.4251	5	5.2	1.2
6	148.26	0.91	760	773.68	298	294	1.1409	-0.4251	5	5.2	0.3
7	147	0.35	760	771.4	298	288	1.1409	-0.4251	5	5.2	0.3
8	147.16	0.01	760	777.48	298	286	1.1409	-0.4251	5	5.1	0.3
9	147.11	0.78	760	772.16	298	287	1.1409	-0.4251	5	5.1	0.3
10	147.82	0.51	760	772.16	298	286	1.1409	-0.4251	5	5.1	0.3
11	148.04	0.39	760	782.8	298	285	1.1409	-0.4251	5	5.1	0.3
12	147.77	0.17	760	772.92	298	282	1.1409	-0.4251	5	5.1	0.3
13	148.93	1.1	760	770.64	298	300	1.1409	-0.4251	5	5.3	0.3
14	147.09	0.06	760	770.64	298	291	1.1409	-0.4251	5	5.2	0.3
15	147.44	0.18	760	769.88	298	289	1.1409	-0.4251	5	5.2	0.2
16	148.09	0.53	760	771.4	298	288	1.1409	-0.4251	5	5.2	0.3
17	148.77	2.53	760	770.64	298	291	1.1409	-0.4251	5	5.2	0.3
18	148.61	1.39	760	769.12	298	293	1.1409	-0.4251	5	5.2	0.3

Appendix 2: Wood sampling

First sampling Campaign

Sample no	Sample source	Sample mass	Sample M.D preparation	Final volume (ml)	Cr (ppm)	Cu (ppm)	As (ppm)	Cr (mg/kg)	Cu (mg/kg)	As (mg/kg)	CCA category (Cr)	CCA category (Cu)	CCA category (As)	Hazard class
1	Nyanga	0.2539	10ml of HNO_3 +5ml of water	25	0.26	0.29	0.11	28.8	11.0	25.5	undetected	undetected	undetected	None
2	Nyanga	0.2527	10ml of HNO_3 +5ml of water	25	0.05	0.28	0.12	27.3	11.5	4.9	undetected	undetected	undetected	None
3	Nyanga	0.2528	10ml of HNO_3 +5ml of water	25	0.02	0.66	0.09	65.5	8.6	1.5	undetected	undetected	undetected	None
4	Nyanga	0.2508	10ml of HNO_3 +5ml of water	25	0.01	0.18	0.09	18.3	8.9	0.6	undetected	undetected	undetected	None
5	Nyanga	0.2514	10ml of HNO_3 +5ml of water	25	0.02	0.43	0.13	42.8	12.9	2.3	undetected	undetected	undetected	None
6	Nyanga	0.2511	10ml of HNO_3 +5ml of water	25	0.02	0.06	0.07	5.5	6.7	2.4	undetected	undetected	undetected	None
7	Nyanga	0.2540	10ml of HNO_3 +5ml of water	25	0.01	0.32	0.09	31.9	8.8	0.8	undetected	undetected	undetected	None
8	Nyanga	0.2506	10ml of HNO_3 +5ml of water	25	0.01	0.21	0.08	20.9	7.6	0.5	undetected	undetected	undetected	None
9	Nyanga	0.2514	10ml of HNO_3 +5ml of water	25	0.00	0.12	0.05	12.3	5.3	0.1	undetected	undetected	undetected	None
10	Nyanga	0.2525	10ml of HNO_3 +5ml of water	25	0.01	0.09	0.05	9.0	5.2	1.4	undetected	undetected	undetected	None
11	Nyanga	0.2502	10ml of HNO_3 +5ml of water	25	0.01	0.18	0.05	17.5	5.0	0.9	undetected	undetected	undetected	None

12	Nyanga	0.2528	10ml of HNO_3 +5ml of water	25	0.00	0.30	0.06	29.7	5.7	0.4	undetected	undetected	undetected	None
13	Nyanga	0.2548	10ml of HNO_3 +5ml of water	25	0.12	0.66	0.09	65.2	8.5	11.5	undetected	undetected	undetected	None
14	Nyanga	0.2554	10ml of HNO_3 +5ml of water	25	0.10	0.32	0.09	31.0	8.5	10.0	undetected	undetected	undetected	None
15	Nyanga	0.2544	10ml of HNO_3 +5ml of water	25	0.09	0.20	0.05	20.0	4.8	8.6	undetected	undetected	undetected	None
16	Nyanga	0.2531	10ml of HNO_3 +5ml of water	25	0.08	0.30	0.04	29.7	4.4	8.0	undetected	undetected	undetected	None
17	Nyanga	0.2578	10ml of HNO_3 +5ml of water	25	0.08	0.19	0.05	18.0	4.9	7.4	undetected	undetected	undetected	None
18	Nyanga	0.2555	10ml of HNO_3 +5ml of water	25	0.07	0.17	0.10	17.1	10.1	7.1	undetected	undetected	undetected	None
19	Nyanga	0.2524	10ml of HNO_3 +5ml of water	25	0.08	0.07	0.04	6.5	3.5	7.5	undetected	undetected	undetected	None
20	Nyanga	0.2543	10ml of HNO_3 +5ml of water	25	0.09	0.17	0.05	16.4	4.9	8.4	undetected	undetected	undetected	None
21	Nyanga	0.2534	10ml of HNO_3 +5ml of water	25	0.07	0.06	0.03	6.1	3.3	6.5	undetected	undetected	undetected	None
22	Nyanga	0.2540	10ml of HNO_3 +5ml of water	25	0.08	0.11	0.09	10.5	8.8	8.3	undetected	undetected	undetected	None
23	Nyanga	0.2536	10ml of HNO_3 +5ml of water	25	0.08	0.37	0.04	36.1	4.2	8.1	undetected	undetected	undetected	None
24	Nyanga	0.2534	10ml of HNO_3 +5ml of water	25	0.08	0.16	0.05	15.3	5.1	8.0	undetected	undetected	undetected	None
25	Nyanga	0.2566	10ml of HNO_3 +5ml of water	25	0.08	0.11	0.08	10.9	7.8	7.5	undetected	undetected	undetected	None
26	Nyanga	0.2531	10ml of HNO_3 +5ml of water	25	0.07	0.01	0.05	1.4	5.2	7.3	undetected	undetected	undetected	None
27	Nyanga	0.2560	10ml of HNO_3 +5ml of water	25	0.07	0.06	0.04	5.5	4.1	6.5	undetected	undetected	undetected	None

28	Nyanga	0.2530	10ml of HNO_3 +5ml of water	25	0.08	0.07	0.15	7.0	15.2	7.8	undetected	undetected	undetected	None
29	Nyanga	0.2532	10ml of HNO_3 +5ml of water	25	0.07	0.19	0.21	18.9	20.5	6.6	undetected	undetected	undetected	None
30	Nyanga	0.2533	10ml of HNO_3 +5ml of water	25	0.08	0.02	0.07	2.4	6.5	7.4	undetected	undetected	undetected	None
31	Nyanga	0.2513	10ml of HNO_3 +5ml of water	25	0.07	0.03	0.02	2.5	2.2	6.7	undetected	undetected	undetected	None
32	Nyanga	0.2547	10ml of HNO_3 +5ml of water	25	0.08	0.06	0.03	6.1	3.0	8.0	undetected	undetected	undetected	None
33	Nyanga	0.2528	10ml of HNO_3 +5ml of water	25	0.08	0.06	0.03	6.2	2.5	7.7	undetected	undetected	undetected	None
34	Nyanga	0.2527	10ml of HNO_3 +5ml of water	25	0.07	0.05	0.06	5.0	6.0	6.7	undetected	undetected	undetected	None
35	Nyanga	0.2555	10ml of HNO_3 +5ml of water	25	0.08	0.04	0.03	3.8	2.6	8.0	undetected	undetected	undetected	None
36	Nyanga	0.2555	10ml of HNO_3 +5ml of water	25	0.08	0.35	0.06	34.3	5.7	7.8	undetected	undetected	undetected	None
37	Nyanga	0.2558	10ml of HNO_3 +5ml of water	25	0.08	0.18	0.06	17.4	5.9	7.7	undetected	undetected	undetected	None
38	Nyanga	0.2525	10ml of HNO_3 +5ml of water	25	0.06	0.09	0.02	8.8	2.5	5.6	undetected	undetected	undetected	None
39	Nyanga	0.2552	10ml of HNO_3 +5ml of water	25	0.08	0.02	0.02	1.7	1.7	7.8	undetected	undetected	undetected	None
40	Nyanga	0.2517	10ml of HNO_3 +5ml of water	25	0.07	0.03	0.03	2.8	2.6	6.7	undetected	undetected	undetected	None
41	Nyanga	0.2527	10ml of HNO_3 +5ml of water	25	0.08	0.11	0.03	10.8	3.3	7.4	undetected	undetected	undetected	None
42	Nyanga	0.2536	10ml of HNO_3 +5ml of water	25	0.06	0.03	0.02	2.6	1.9	6.1	undetected	undetected	undetected	None
43	Nyanga	0.2516	10ml of HNO_3 +5ml of water	25	0.06	0.07	0.05	7.3	4.6	6.0	undetected	undetected	undetected	None

44	Nyanga	0.2533	10ml of HNO_3 +5ml of water	25	0.07	0.03	0.02	2.6	2.3	7.0	undetected	undetected	undetected	None

45	Nyanga	0.2540	10ml of HNO_3 +5ml of water	25	0.07	0.07	0.02	7.2	1.8	7.0	undetected	undetected	undetected	None
46	Nyanga	0.2540	10ml of HNO_3 +5ml of water	25	0.07	0.03	0.03	3.2	3.0	7.3	undetected	undetected	undetected	None
47	Nyanga	0.2540	10ml of HNO_3 +5ml of water	25	0.09	0.02	0.03	1.5	3.2	8.9	undetected	undetected	undetected	None
48	Nyanga	0.2560	10ml of HNO_3 +5ml of water	25	0.07	0.05	0.12	4.6	11.8	7.3	undetected	undetected	undetected	None
49	Nyanga	0.2553	10ml of HNO_3 +5ml of water	25	0.09	0.12	0.05	12.1	4.9	8.9	undetected	undetected	undetected	None
50	Nyanga	0.2552	10ml of HNO_3 +5ml of water	25	0.07	0.06	0.15	5.4	15.1	7.1	undetected	undetected	undetected	None
51	Nyanga	0.2527	10ml of HNO_3 +5ml of water	25	0.08	0.03	0.03	2.7	2.6	8.0	undetected	undetected	undetected	None
52	Nyanga	0.2543	10ml of HNO_3 +5ml of water	25	0.09	0.04	0.04	3.4	3.5	8.6	undetected	undetected	undetected	None
53	Nyanga	0.2527	10ml of HNO_3 +5ml of water	25	0.08	0.02	0.03	2.0	3.1	7.6	undetected	undetected	undetected	None
54	Nyanga	0.2540	10ml of HNO_3 +5ml of water	25	0.09	0.04	0.05	4.2	5.0	8.9	undetected	undetected	undetected	None
55	Nyanga	0.2535	10ml of HNO_3 +5ml of water	25	0.08	0.04	0.00	4.0	0.4	7.6	undetected	undetected	undetected	None
56	Khayelitsha	0.2560	10ml of HNO_3 +5ml of water	25	0.07	0.08	0.01	7.5	0.7	6.9	undetected	undetected	undetected	None
57	Khayelitsha	0.2538	10ml of HNO_3 +5ml of water	25	0.04	0.09	0.03	8.5	2.6	3.8	undetected	undetected	undetected	None
58	Khayelitsha	0.2552	10ml of HNO_3 +5ml of water	25	0.05	0.10	0.01	9.6	0.6	5.4	undetected	undetected	undetected	None

59	Khayelitsha	0.2552	10ml of HNO_3+5ml of water	25	0.06	0.10	0.01	10.2	1.0	5.6	undetected	undetected	undetected	None
60	Khayelitsha	0.2556	10ml of HNO_3+5ml of water	25	0.07	0.07	0.01	7.0	0.8	6.5	undetected	undetected	undetected	None
61	Khayelitsha	0.2552	10ml of HNO_3+5ml of water	25	0.06	0.11	0.02	11.2	2.0	5.9	undetected	undetected	undetected	None
62	Khayelitsha	0.2552	10ml of HNO_3+5ml of water	25	0.06	0.09	0.01	9.2	1.2	6.0	undetected	undetected	undetected	None
63	Khayelitsha	0.2548	10ml of HNO_3+5ml of water	25	0.09	0.12	0.04	11.6	3.7	8.8	undetected	undetected	undetected	None
64	Khayelitsha	0.2542	10ml of HNO_3+5ml of water	25	0.07	0.11	0.03	11.0	3.3	6.5	undetected	undetected	undetected	None
65	Khayelitsha	0.2540	10ml of HNO_3+5ml of water	25	0.04	0.10	0.02	10.1	1.7	4.3	undetected	undetected	undetected	None
66	Khayelitsha	0.2542	10ml of HNO_3+5ml of water	25	0.06	0.17	0.01	16.8	0.9	6.3	undetected	undetected	undetected	None
67	Khayelitsha	0.2530	10ml of HNO_3+5ml of water	25	0.04	0.08	0.14	8.2	14.2	4.4	undetected	undetected	undetected	None
68	Khayelitsha	0.2549	10ml of HNO_3+5ml of water	25	0.05	0.14	0.03	14.0	3.3	5.3	undetected	undetected	undetected	None
69	Khayelitsha	0.2547	10ml of HNO_3+5ml of water	25	0.06	0.08	0.01	7.9	0.8	6.0	undetected	undetected	undetected	None
70	Khayelitsha	0.2520	10ml of HNO_3+5ml of water	25	0.07	0.14	0.27	13.6	26.9	6.5	undetected	undetected	undetected	None
71	Khayelitsha	0.2537	10ml of HNO_3+5ml of water	25	0.06	0.09	0.04	8.7	4.0	6.1	undetected	undetected	undetected	None
72	Khayelitsha	0.2530	10ml of HNO_3+5ml of water	25	0.09	0.10	0.06	10.0	5.9	8.5	undetected	undetected	undetected	None
73	Khayelitsha	0.2550	10ml of HNO_3+5ml of water	25	0.06	0.07	0.03	7.3	2.6	6.2	undetected	undetected	undetected	None
74	Khayelitsha	0.2537	10ml of HNO_3+5ml of water	25	0.08	0.12	0.04	11.8	4.0	7.9	undetected	undetected	undetected	None
75	Khayelitsha	0.2585	10ml of HNO_3+5ml of water	25	0.05	0.10	0.02	9.3	1.9	4.9	undetected	undetected	undetected	None

76	Khayelitsha	0.2560	10ml of HNO_3 +5ml of water	25	0.05	0.07	0.01	6.9	0.6	4.4	undetected	undetected	undetected	None
77	Khayelitsha	0.2583	10ml of HNO_3 +5ml of water	25	0.06	0.02	-0.01	1.6	-0.9	5.7	undetected	undetected	undetected	None
78	Khayelitsha	0.2585	10ml of HNO_3 +5ml of water	25	0.05	0.08	0.00	7.4	0.2	4.5	undetected	undetected	undetected	None
79	Khayelitsha	0.2543	10ml of HNO_3 +5ml of water	25	0.06	0.08	0.01	7.7	0.6	5.8	undetected	undetected	undetected	None
80	Khayelitsha	0.2562	10ml of HNO_3 +5ml of water	25	0.05	0.02	-0.01	1.6	-1.0	5.0	undetected	undetected	undetected	None
81	Khayelitsha	0.2532	10ml of HNO_3 +5ml of water	25	0.04	0.08	0.00	7.7	0.3	4.3	undetected	undetected	undetected	None
82	Khayelitsha	0.2581	10ml of HNO_3 +5ml of water	25	0.06	0.09	0.01	8.4	0.6	5.4	undetected	undetected	undetected	None
83	Khayelitsha	0.2516	10ml of HNO_3 +5ml of water	25	0.05	0.01	-0.01	1.2	-0.8	5.1	undetected	undetected	undetected	None
84	Khayelitsha	0.2570	10ml of HNO_3 +5ml of water	25	0.04	0.00	-0.01	0.1	-0.8	3.5	undetected	undetected	undetected	None
85	Khayelitsha	0.2537	10ml of HNO_3 +5ml of water	25	0.05	0.07	-0.01	7.3	-1.0	5.1	undetected	undetected	undetected	None
86	Khayelitsha	0.2526	10ml of HNO_3 +5ml of water	25	0.05	0.10	0.00	10.4	0.2	5.2	undetected	undetected	undetected	None

Second sampling campaign

Sample number	Sample source	Sample mass	Sample M.D preparation	Final volume (ml)	Cr (ppm)	Cu (ppm)
1	Stellenbosch	0.2584	10ml of HNO_3 +5ml of water	25	66.54	17.69
2	Worcester	0.2566	10ml of HNO_3 +5ml of water	25	5.25	5.26
3	Worcester	0.2516	10ml of HNO_3 +5ml of water	25	16.77	9.91
4	Worcester	0.2503	10ml of HNO_3 +5ml of water	25	0.44	-0.03
5	Worcester	0.2510	10ml of HNO_3 +5ml of water	25	6.66	3.89
6	Worcester	0.2521	10ml of HNO_3 +5ml of water	25	7.93	4.51
7	Worcester	0.2570	10ml of HNO_3 +5ml of water	25	11.59	6.63
8	Worcester	0.2538	10ml of HNO_3 +5ml of water	25	5.44	3.23
9	Worcester	0.2541	10ml of HNO_3 +5ml of water	25	0.21	-0.06
10	Mbekweni	0.2547	10ml of HNO_3 +5ml of water	25	0.06	-0.13
11	Mbekweni	0.2523	10ml of HNO_3 +5ml of water	25	38.80	18.05
12	Mbekweni	0.2519	10ml of HNO_3 +5ml of water	25	0.51	0.14

Sample number	As (ppm)	Cr (mg/kg)	Cu (mg/kg)	As (mg/kg)	CCA category (Cr)	CCA category (Cu)	CCA category (As)	Hazard class
1	36.50	6437.7	1711.5	3531.3	6437.69	1711.49	3531.35	**H5**
2	5.14	511.0	512.4	501.1	511.01	512.35	501.05	**H2**
3	16.03	1666.3	984.3	1592.6	1666.34	984.28	1592.61	**H4**
4	0.10	43.5	-3.3	10.2	undetected	undetected	undetected	_
5	6.70	662.9	387.6	666.9	662.87	387.58	666.92	**H2**
6	6.92	786.6	447.5	686.5	786.62	447.54	686.53	**H2**

7	11.18	1127.1	645.2	1087.1	1127.14	645.20	1087.06	H3
8	4.89	535.4	317.8	481.2	535.38	317.80	481.21	H2
9	0.07	21.0	-6.3	6.4	undetected	undetected	undetected	_
10	-0.02	5.6	-12.5	-1.5	undetected	undetected	undetected	_
11	28.98	3844.2	1788.4	2871.4	3844.23	1788.45	2871.38	H5
12	0.34	50.2	14.2	33.5	undetected	undetected	undetected	_

Third sampling campaign

Sample number	Sample source	Sample mass	Sample M.D preparation	Final volume (ml)	Cr (ppm)
1	langa (last sample)	0.2562	10ml of HNO_3+5ml of water	25	-0.04
2	langa(filter12)	0.2587	10ml of HNO_3+5ml of water	25	-0.08
3	langa zone 24,no 4(IC)	0.2582	10ml of HNO_3+5ml of water	25	22.84
4	langa,braai(2C)	0.2512	10ml of HNO_3+5ml of water	25	0.04
5	langa,braai(3C)	0.2541	10ml of HNO_3+5ml of water	25	0.02
6	khayelitsha1(4C)	0.2503	10ml of HNO_3+5ml of water	25	2.76
7	Khayelitsha2(5C)	0.2517	10ml of HNO_3+5ml of water	25	13.99
8	khayelitsha(sheeps head)	0.2555	10ml of HNO_3+5ml of water	25	30.28
9	nyanga(chicken boiler)	0.2550	10ml of HNO_3+5ml of water	25	-0.06
10	nyanga (beer vendor)	0.2591	10ml of HNO_3+5ml of water	25	0.12
11	nyanga braai(start fire)	0.2537	10ml of HNO_3+5ml of water	25	25.81
12	nyanga(sheep vendor)	0.2582	10ml of HNO_3+5ml of water	25	13.3
13	nyanga(chicken boiler)	0.2555	10ml of HNO_3+5ml of water	25	-0.03
14	nyanga(chicken boiler)	0.2520	10ml of HNO_3+5ml of water	25	0.57

15	Stellenbosch1(6C)	0.2586	10ml of HNO_3+5ml of water	25	0.02
16	Stellenbosch(chicken boiler)	0.2548	10ml of HNO_3+5ml of water	25	35.85
17	Stellenbosch(chicken boiler)	0.2545	10ml of HNO_3+5ml of water	25	14.41
18	Stellenbosch(chicken boiler)	0.2593	10ml of HNO_3+5ml of water	25	9.85

Sample number	Cu (ppm)	As (ppm)	Cr (mg/kg)	Cu (mg/kg)	As (mg/kg)	CCA category (Cr)	CCA category (Cu)	CCA category (As)	Hazard class
1	-0.05	-0.03	-3.9	-4.9	-2.9	undetected	undetected	undetected	_
2	-0.08	-0.07	-7.7	-7.7	-6.8	undetected	undetected	undetected	_
3	9.83	19.29	2211.5	951.8	1867.7	2211.46	951.78	1867.74	H4
4	0.02	0.09	4.0	2.0	9.0	undetected	undetected	undetected	_
5	0	0.09	2.0	0.0	8.9	undetected	undetected	undetected	_
6	0.06	0.19	275.7	6.0	19.0	275.67	undetected	undetected	_
7	7.08	12.79	1389.6	703.2	1270.4	1389.55	703.22	1270.36	H3
8	15.12	27.38	2962.8	1479.5	2679.1	2962.82	1479.45	2679.06	H5
9	-0.03	-0.04	-5.9	-2.9	-3.9	undetected	undetected	undetected	_
10	0.1	0.09	11.6	9.6	8.7	undetected	undetected	undetected	_
11	10.22	20.58	2543.4	1007.1	2028.0	2543.36	1007.09	2027.99	H4
12	5.89	10.1	1287.8	570.3	977.9	1287.76	570.29	977.92	H2
13	0.03	-0.01	-2.9	2.9	-1.0	undetected	undetected	undetected	_
14	0.29	0.21	56.5	28.8	20.8	undetected	undetected	undetected	_
15	0.02	0.06	1.9	1.9	5.8	undetected	undetected	undetected	_
16	12.02	24.97	3517.5	1179.4	2450.0	3517.46	1179.36	2449.96	H5
17	5.7	11.23	1415.5	559.9	1103.1	1415.52	559.92	1103.14	H3
18	5.38	8.13	949.7	518.7	783.8	949.67	518.70	783.84	H2

Appendix 3: Ethics form

EBE Faculty: Assessment of Ethics in Research Projects

Any person planning to undertake research in the Faculty of Engineering and the Built Environment at the University of Cape Town is required to complete this form before collecting or analysing data. When completed it should be submitted to the supervisor (where applicable) and from there to the Head of Department.
If any of the questions below have been answered YES, and the applicant is NOT a fourth year student, the Head should forward this form for approval by the Faculty EIR committee: submit to Ms Zulpha Geyer - Zulpha.Geyer@uct.ac.za; Chemical Engineering Building, Upper Campus, UCT, (Ph 021 650 4791)
NB: A copy of this completed form must be included with the thesis/dissertation/report when it is submitted for examination.

Name of Principal Researcher/Student: [illegible] Department: Chemical Engineering

Preferred email address of applicant: [illegible]

If a Student: Degree: Masters Supervisor: A Prof Harro Von Blottnitz

If a Research Contract: indicate source of funding/sponsorship

Research Project Title: Investigation of metal mobilization from the use of CCA (Chromated Copper Arsenate) treated timber.

Overview of ethics issues in your research project:

Question 1: Is there a possibility that your research could cause harm to a third party (i.e. a person not involved in your project)?	YES	NO ✓
Question 2: Is your research making use of human subjects as sources of data? If your answer is YES, please complete Addendum 2.	YES ✓	NO
Question 3: Does your research involve the participation of or provision of services to communities? If your answer is YES, please complete Addendum 3.	YES ✓	NO
Question 4: If your research is sponsored, is there any potential for conflicts of interest? If your answer is YES, please complete Addendum 4.	YES	NO ✓

If you have answered YES to any of the above questions, please append a copy of your research proposal, as well as any interview schedules or questionnaires (Addendum 1) and please complete further addenda as appropriate.

I hereby undertake to carry out my research in such a way that

- there is no apparent legal objection to the nature or the method of research, and
- the research will not compromise staff or students or the other responsibilities of the University,
- the stated objective will be achieved, and the findings will have a high degree of validity;
- limitations and alternative interpretations will be considered;
- the findings could be subject to peer review and publicly available; and,
- I will comply with the conventions of copyright and avoid any practice that would constitute plagiarism

Signed by	Full name and signature	Date
Principal Researcher/Student:		

This application is approved by

Supervisor (if applicable):		
HOD (or delegated nominee): Final authority for all assessments with NO to all questions and for all undergraduate research.		
Chair - Faculty EIR Committee: For applicants other than undergraduate students who have answered YES to any of the above questions.		

It is assumed that you have read the UCT Code for Research involving Human Subjects (available at http://web.uct.ac.za/depts/educate/downloads/uctcodeforresearchinvolvinghumansubjects.pdf) in order to be able to answer the questions in this addendum

2.1 Does the research discriminate against participation by individuals or differentiate between participants on the grounds of gender, race or ethnic group, age range, religion, income, handicap, illness or any similar classification?	YES ✓	NO
2.2 Does the research require the participation of socially or physically vulnerable people (children, aged, disabled, etc) or legally restricted groups?	YES	NO ✓
2.3 Will you not be able to secure the informed consent of all participants in the research? (In the case of children, will you not be able to obtain the consent of their guardians or parents?)	YES	NO ✓
2.4 Will any confidential data be collected or will identifiable records of individuals be kept?	YES	NO ✓
2.5 In reporting on this research is there any possibility that you will not be able to keep the identities of the individuals involved anonymous?	YES	NO ✓
2.6 Are there any foreseeable risks of physical, psychological or social harm to participants that might occur in the course of the research?	YES	NO ✓
2.7 Does the research include making payments or giving gifts to any participants?	YES	NO ✓

If you have answered YES to any of these questions, please describe below how you plan to address these issues

2.1. This research involves "cattle" who use the word as a tool to prepare meat and sheep head. We only need them to give us some piece of wood

3.1 Is the community expected to make decisions for, during or based on the research?	YES	NO ✓
3.2 At the end of the research will any economic or social process be terminated or left unsupported, or equipment or facilities used in the research be recovered from the participants or community?	YES	NO ✓
3.3 Will any service be provided at a level below the generally accepted standards?	YES	NO ✓

If you have answered YES to any of these questions, please describe below how you plan to address these issues

⇒ We only need the community (Cattlemen) to give us some pieces of wood and allocate us to set up our air samplers close to their working place.